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FOR
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
DEPT. OF HEALTH, EDUCATION & WELFARE
CONTRACT NUMBER PH 86-68-48

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SUBMITTED BY
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A novel process for the removal of sulfur dioxide from waste gases is described. In this process, SO_2 is directly reduced to elemental sulfur by hydrogen sulfide which is in turn generated by reducing part of the elemental sulfur with natural gas. The objectives of the study made on this process are as follows: to demonstrate the feasibility of each process step; to construct and operate an integrated pilot plant using a real flue gas; and to develop design and economic data for full scale application to various waste gas streams.

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October 19, 1967 - July 30, 1969

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

FINAL REPORT

TABLE OF CONTENTS

Section		Page
	Foreword	ii
I.	Introduction	1
II.	Summary	8
III.	Bench Scale Investigations	45
IV.	Pilot Plant Design, Construction and Operation	106
V.	Process Design and Economics	159
VI.	Literature Review	203
VII.	Appendix	227

FOREWORD

This report describes work conducted by Princeton Chemical Research, Inc. under Contract No. PH-86-68-48, on the development of a novel process for the removal of sulfur dioxide from waste gases. In this process, sulfur dioxide is directly reduced to elemental sulfur by hydrogen sulfide which is in turn generated by reducing part of the elemental sulfur with natural gas.

The objectives of this contract have been three-fold: to demonstrate the feasibility of each process step; to construct and operate an integrated pilot plant using a real flue gas; and to develop design and economic data for full scale application to various wastegas streams.

As a result of this contract, the process technology is considered to be in an advanced state, with the feasibility and partial scale-up of each step demonstrated. A process design which appears to be feasible and economic has been developed, although additional pilot plant data and engineering development are required.

Because of the attractive technical and economic features, it is concluded that the present process is one of the most promising control methods for sulfur dioxide emissions. It is strongly recommended that development of the process be continued.

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION I

INTRODUCTION

TABLE OF CONTENTS

SECTION I - INTRODUCTION

Page

1. History of Project 3
2. Process Concept 3
3. Attractive Features 5
4. Personnel and Acknowledgments 6

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION I - INTRODUCTION

1. History of Project

The proposed process was conceived at PCR early in 1967. It was presented informally to NAPCA representatives in May, 1967. As a result of this presentation, PCR submitted an unsolicited proposal for a bench scale project to begin developing the concept. A nine-month cost plus fixed fee contract was awarded in October, 1967.

This first phase demonstrated the technical feasibility and indicated the possibility of favorable economics.

In the spring of 1968, a proposal to extend the work into a pilot plant stage was made. The proposal was accepted, and the original contract was extended for twelve months. This second phase included the design, construction, and operation of a continuous integrated pilot plant as well as concurrent laboratory support work.

In 1968, a British Patent (1,097,306) was issued to Peter Spence & Sons, Limited, for the dilute concentration, low temperature version of Claus process. The corresponding patent has not issued in the United States.

This report covers the work carried out during the twenty-one months of NAPCA funding.

2. Process Concept

The main technical features of the process are:

(a) Sulfur dioxide (SO_2) is catalytically reduced in one step to elemental sulfur, using hydrogen sulfide (H_2S).

(b) The H_2S is generated by the one step reaction of elemental sulfur with natural gas and water. No hydrogen is required.

(c) The reduction and sulfur collection are performed near normal flue gas temperature.

(d) Removal of nitrogen oxides is thermodynamically possible.

The concept gives promise of attractive economics:

(a) Low investment and operating costs before by-product credits.

(b) Breakeven possibilities with credit for by-product sulfur.

(c) Recovery of elemental sulfur by-product, the most desirable form of sulfur because of its ease of storing, handling, shipping, and marketing.

The process is based on the reduction of SO_2 to elemental sulfur by a modified Claus reaction:

$$2H_2S + SO_2 \rightleftharpoons \frac{3}{X} S_X + 2H_2O$$

The low concentration of sulfur dioxide, the high oxygen and water content, and the economic limitation on heating and cooling waste gases require this reaction to be carried out under conditions very different from the Claus sulfur recovery process.

To avoid the use of expensive hydrogen, the process produces the H_2S by the reaction of natural gas (or other hydrocarbons) and water with part of the sulfur produced by the reduction:

$$\frac{1}{2}CH_4 + H_2O + \frac{2}{X} S_X \longrightarrow 2H_2S + \frac{1}{2}CO_2$$

The high reactivity of the hydrogen sulfide allows reduction of the sulfur dioxide at relatively low temperatures (200-400°F). This is important because, at these low temperatures:

(a) Oxygen present in many SO_2 containing waste gases does not cause interfering oxidation reactions.

(b) Water present in many SO_2 containing waste gases does not limit conversion by equilibrium.

(c) No serious economic debit is incurring for heating and cooling the gas.

The process therefore has potential for reducing sulfur dioxide (or hydrogen sulfide) emissions from various sources, for example:

(a) Fossil fuel power plants
(b) Metallurgical roasting plants (smelters)
(c) Oil refineries
(d) Sulfuric acid plants
(e) Claus sulfur plants
(f) Pulp and paper manufacturing

3. Attractive Features

The process produces a by-product, elemental sulfur, which can provide major credits to offset operating costs. Under certain conditions, profit possibilities exist. Elemental sulfur is a more attractive by-product than sulfuric acid, sulfur dioxide, hydrogen sulfide, sulfates, and sulfites produced in other processes because of the ease of storage, economics of shipping, and other marketing considerations.

No waste disposal problem is created.

Natural gas is the only raw material required. Although natural gas is inexpensive, and usually available, other paraffinic fuels such as liquified petroleum gas (LPG) should be suitable alternatives.

Low investment and operating costs are possible because operations carried out on the flue gas are limited to a small amount of compression and passage through a catalyst bed - at or near flue gas temperatures. The sulfur produced is collected on the catalyst, and no major flue gas heating, cooling, or collection equipment is required. The balance of the process equipment operates on much smaller streams.

The process has the thermodynamic potential of concurrently removing nitrogen oxides, reducing them to nitrogen by reaction with the hydrogen sulfide.

4. Personnel and Acknowledgments

The contributions of PCR employees, equipment and material suppliers, and NAPCA personnel are hereby acknowledged with thanks. Special note should be made of the contributions of the following:

(a) George Huffman, NAPCA Project officer, for maintaining good communication and working relationships between NAPCA and PCR.

(b) North American Mfg. Company (especially Mr. Harold Gonering) for help in bringing the coal burner on stream.

(c) Consolidation Coal Company for providing the coal at no charge to PCR or NAPCA.

(d) Matthey Bishop Company for providing, at no cost, catalyst for the pilot plant exhaust cleanup system.

A list of PCR personnel may be found as Table I-1. The suppliers of major pilot plant items are listed in Section IV.

The report was prepared by R. F. Toro, J. Magder, and A. T. Goding.

TABLE I-1

PCR PERSONNEL

Project Director - Original - Dr. N. J. Weinstein
Successor - Mr. R. F. Toro

Professionals

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REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION II

SUMMARY

TABLE OF CONTENTS

SECTION II - SUMMARY

Page

1. Process Summary 12
2. Technology 13
    - 2.1 SO_2 Reduction with H_2S 14
        - 2.11 Operating Conditions 15
        - 2.12 Catalyst Activity 15
        - 2.13 Catalysts 16
        - 2.14 Effects of Flue Gas Composition 17
    - 2.2 H_2S Generation 19
3. State of Development 20
    - 3.1 Pilot Plant Design, Construction and Operation 20
    - 3.2 SO_2 Reduction 22
        - 3.21 Catalysts 22
        - 3.22 Scale-up 22
        - 3.23 Reaction Control 24
        - 3.24 Reactor Design 24
        - 3.25 Materials of Construction 25
        - 3.26 Effects of Flue Gas Composition 25
    - 3.3 H_2S Generation 26
        - 3.31 Catalysts 26
        - 3.32 Scale-up 26
        - 3.33 Reactor Design and Materials of Construction 26
4. Projected Economics 27
    - 4.1 Process Design 27
    - 4.2 Investment and Operating Costs 28
    - 4.3 Sensitivity of Economics 29

LIST OF TABLES

SECTION II - SUMMARY

Table	Title	Page
II-1	Equilibrium Limitation of H_2S-SO_2 Reaction and Effects of Oxygen at High Temperature	30
II-2	Typical Conditions for High H_2S-SO_2 Conversions	31
II-3	Typical Results of SO_2 Reduction in Smelter Gas	32
II-4	Conversions vs. Catalyst Sulfur Loading	33
II-5	Catalyst Deactivation During Sulfur Stripping With N_2	34
II-6	Restoration of Catalyst Activity by Contact With H_2S at High Temperature	35
II-7	Catalysts Found Effective for SO_2-H_2S Reaction	36
II-8	Effects of Nitrogen Oxides on H_2S and SO_2 Conversions	37
II-9	H_2S Generation Data	38
II-10	Typical Comparison of Pilot Plant and Lab Data - SO_2 Reduction	39
II-11	H_2S Emission Control Data	40
II-12	Typical Comparison of Pilot Plant and Lab Data - H_2S Generation	41

LIST OF FIGURES

SECTION II - SUMMARY

Figure	Title	Page
II-1	Economic Effects of Sulfur Content of Coal	42
II-2	Economic Effects of Power Plant Size	43
II-3	Economic Effects of Operating Factor and Catalyst Cost	44

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION II - SUMMARY

1. Process Summary

Significant progress has been made in advancing the technology required to apply the "Claus reaction":

$$2H_2S + SO_2 \xrightarrow{\text{Catalyst}} 2H_2O + \frac{3}{X} S_X$$

to the problem of removing sulfur dioxide from the waste gases of power plants, smelters, and other plants.

Two problems of catalyst deactivation experienced by others were met and solved:

(a) Between catalyst regenerations with hot inert gas, a steady decline in catalyst activity was overcome by a novel regeneration technique. Inert gas (N_2) containing at least as little as 5% H_2S was found to completely restore catalyst activity.

(b) In the presence of nitrogen oxides, activated alumina experienced a severe and steady decline of activity during the reduction of SO_2. Attributed by others to chloride, this deactivation was determined to be caused by NO_x, and avoided by the use of 13X molecular sieves.

Concern over excessive H_2S emissions from such a process appears to be without merit. Control of the emissions to permissible levels seems likely. Even with excess H_2S, experimental data show emissions are not excessive.

A process design which appears to be feasible and economic has been developed, although further engineering development is required.

Existing methods of generating H_2S were an economic bar to the commercial use of the process. Conventional techniques of producing H_2S (hydrogen produced by reforming plus sulfur, or methane plus sulfur) suffered because hydrogen generation is very expensive and carbon disulfide is unreactive with SO_2 and is therefore an expensive by-product.

A novel route to generating H_2S in near theoretical yields has been developed:

$$\tfrac{1}{2}CH_4 + \frac{2}{X} S_X + H_2O \longrightarrow \tfrac{1}{2}CO_2 + 2H_2S \ .$$

The cost of the equipment for this step of the process is a very small fraction of the total process costs. The H_2S generation step may have utility in the chemical industry as a process in itself.

2. Technology

The program investigations included study of the SO_2 reduction reaction,

$$2H_2S + SO_2 \xrightarrow{\text{Catalyst}} 2H_2O + \frac{3}{X} S_X \qquad \text{vapor phase}$$

primarily for a power plant situation (0.2-0.3% SO_2, 3% O_2, 15% CO_2, 7% H_2O, 75% N_2). Catalysts, operating conditions, catalyst regeneration, and effects of flue gas composition were studied and optimized.

In a very limited study, CS_2 was tested as a possible replacement for H_2S and found to be unreactive.

A novel method of generating the H_2S from part of the product sulfur was conceived:

$$\tfrac{1}{2}CH_4 + \frac{2}{X} S_X + H_2O \xrightarrow{\text{Catalyst}} \tfrac{1}{2}CO_2 + 2H_2S \quad \text{vapor phase.}$$

Representing an advance over the prior art,

$$CH_4 + \frac{4}{X} S_X \xrightarrow{\text{Catalyst}} CS_2 + 2H_2S \qquad \text{vapor phase}$$

or

$$\tfrac{1}{2}CH_4 + \tfrac{1}{2}H_2O \xrightarrow{\text{Catalyst}} \tfrac{3}{2}H_2 + \tfrac{1}{2}CO \qquad \text{vapor phase}$$

$$\tfrac{1}{2}CO + \tfrac{1}{2}H_2O \xrightarrow{\text{Catalyst}} \tfrac{1}{2}H_2 + \tfrac{1}{2}CO_2 \qquad \text{vapor phase}$$

$$2H_2 + \frac{2}{X} S_X \longrightarrow 2H_2S \qquad \text{vapor phase}$$

the new route requires no expensive hydrogen-producing steps and produces no by-product CS_2 (non-reactive with SO_2 at flue gas conditions). Near theoretical yields were achieved during the optimization program which studied catalysts and operating conditions.

A liquid phase technique and a non-catalytic vapor phase technique were briefly studied, but results were so poor that work was terminated.

2.1 SO_2 Reduction With H_2S

The SO_2 reduction reaction was studied over two temperature ranges. In the higher range (400-500°F), the vapor pressure of sulfur is high enough that the sulfur produced during the reaction does not deposit continuously on the catalyst surface. The sulfur may be recovered by condensing it downstream.

At temperatures below 400-500°F, the sulfur formed deposits continuously on the catalyst, eventually causing the activity (conversions) to fall off. At the lower temperatures, the reaction must be stopped periodically and the sulfur removed from the catalyst.

It was discovered that simple vaporization of the sulfur by hot inert gas did not completely restore the catalyst activity. A technique for concurrently stripping the sulfur off the catalyst and restoring the activity of the catalyst was developed.

A variety of catalysts were examined for suitability for the low temperature SO_2 reduction reaction. The general classes of catalysts studied were activated aluminas, activated carbons, molecular sieves, silica gels, silica-aluminas, and activated bauxites. Most of the catalysts were commercially available, but some specially prepared catalysts were tested.

The catalysts were evaluated for initial activity for SO_2 reduction; if active they were also examined for regenerability after a reduction cycle. The most promising catalysts were further tested for resistance to nitrogen oxides or chloride which are normally present in power plant flue gases in trace quantities.

The majority of the experiments were conducted feeding SO_2 concentrations in power plant flue gases: 0.2-0.3%. A few experiments were carried out on SO_2-N_2 mixtures, but most of the work employed simulated flue gas mixtures of CO_2, O_2, N_2, H_2O and SO_2. Nitrogen dioxide, nitric oxide, and/or hydrogen chloride were added in the experiments studying the effects of trace flue gas components.

The reduction of SO_2 was also demonstrated at higher concentrations. A simulated undiluted smelter gas stream of SO_2 with a small amount of O_2, the balance nitrogen was used.

2.11 Operating Conditions

For the power plant flue gas, temperatures of 200-300°F were required for high conversions. Higher temperatures limited conversions by equilibrium. (See Table II-1). At higher temperatures, oxidation reactions became significant. At these temperatures, 1-2 seconds contact time (1800-3600 V/V/HR space velocity) was found to be adequate. (See Table II-2).

At these temperatures, sulfur condensed on the catalyst, but conversions remained high ($>$ 95%) until the catalyst was loaded to about 25% by weight with sulfur. This corresponded to an onstream time of 6-10 hours. (See Table II-4).

For the undiluted smelter gas, the greater concentration of SO_2 prohibited the low temperature route because the onstream time would be reduced to minutes. For this case, the reductions were carried out at 500-750°F and space velocities of 1400 and 4900 V/V/HR. Although there was not much variation in conversions, 650°F and the higher space velocity appeared to be optimum. Catalyst activity did not change after 60 hours of onstream time with no regeneration procedures. (See Table II-3).

2.12 Catalyst Activity

At the low temperatures (200-300°F), the sulfur which deposited on the catalyst had to be removed in order to restore activity. It could be removed and recovered by stripping it off with inert gas at sulfur vaporizing temperatures. Nitrogen at 950°F worked well. However, catalyst activity was not completely restored after sulfur removal with nitrogen, and continued to drop after each cycle. (See Table II-5).

This deactivation between cycles was believed to be caused by sulfate formation during the reduction and/or stripping steps. A practical solution was developed to overcome this problem. Stripping with nitrogen containing H_2S in concentrations at least as low as 5% completely reactivated the catalyst. (See Table II-6).

Washing of the catalyst with water after stripping resulted in substantial recovery, lending support to the sulfate theory. This technique was not deemed to be practical however.

A list of reactivation techniques which were not successful can be found in Section III-1.112.

At the higher temperatures, steady state reaction conditions prevailed. No drop in catalyst activity was observed after 60 hours of onstream time (16% SO_2 flue gas).

2.13 Catalysts

The following catalysts were found to be good or excellent for the SO_2 reduction at 200-300°F for the power plant flue gas. (See Table II-7).

- Molecular Sieves Type 13X
  - Linde 13X
  - Davison 542
- Activated Aluminas
  - Spence Actal A
  - Matheson, Coleman and Bell AX-610 (Reynolds RA-3)
  - Alcoa H-151
  - Alcoa F-1
  - Conoco Catapal N-2
  - Intsel Grade A (St. Gobain)
- Activated Bauxites
  - Engelhard Porocel Sulfur Recovery Catalyst
  - Engelhard Porocel LPD

A list of catalysts which showed poor or negligible activity can be found as Table III-2.

As noted in paragraph 2.14, the activated aluminas are affected by nitrogen oxides, while the molecular sieves are not. The bauxites were not studied.

At the higher temperatures, only activated alumina was tested. It was found to be suitable.

2.14 Effects of Flue Gas Composition

The concentration of the following gases are considered important:

Oxygen	Nitrogen Oxides
Water	Chlorides
Sulfur Dioxide	Hydrogen Sulfide

The following gases are believed to be inert to the reactions:

Nitrogen	Carbon Dioxide

The effects and disposition of the following gases are not known:

Carbonyl Sulfide	Sulfur Trioxide
Carbon Monoxide	Carbon Disulfide
Methane	

When O_2 and H_2O are present at high temperature (400-500°F) rapid catalyst deactivation and/or low conversions are generally observed. (See Table II-1). Water shifts the equilibrium conversion for the reaction:

$$2H_2S + SO_2 \rightleftharpoons \frac{3}{X} S_X + 2H_2O \quad ,$$

but at low temperatures (200-300°F), the equilibrium is so favorable that the effects of water concentration are very small.

The presence of oxygen at the higher temperatures provides an opportunity for side reactions such as:

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$2SO_2 + 2H_2O + O_2 \longrightarrow 2H_2SO_4$$

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S$$

$$2H_2S + 2O_2 \longrightarrow 2H_2O + 2SO_2$$

$$H_2S + 2O_2 \longrightarrow H_2SO_4 \quad .$$

These side reactions may consume either H_2S or SO_2 and/or deactivate the catalyst (by e.g. sulfate).

The concentration of SO_2 is of importance to equilibrium at higher temperatures. At 16% SO_2, for example, as in undiluted smelter gas, operation at 500-750°F is possible, and 95% conversions can be reached. High concentrations of oxygen however probably cannot be tolerated at these temperatures because of side reactions.

The concentration of H_2S (or H_2S/SO_2 ratio) is important for equilibrium considerations as well as SO_2 conversion, but more importantly because of the residual H_2S remaining in the flue gas. Fortunately, it was found that residual H_2S is less than what would be predicted by equilibrium (or even stoichiometric) calculations. (See Figure III-4). The disappearance of the H_2S probably occurs by reaction with molecular oxygen.

Nitrogen oxides (500 ppm as NO, NO_2 or 90% NO, 10% NO_2) were found to cause rapid and severe deactivation of activated alumina during the SO_2 reduction cycle. Although the high activity can be completely restored by the H_2S/N_2 stripping technique, the deactivation recurs and is continuous. Removal of the NO_X during the reduction results in a reactivation of the catalyst. (See Figure III-3).

Molecular Sieve 13X catalyst was found to be completely resistant to NO_X deactivation. 100 ppm of HCl added to the NO_X containing flue gas had no adverse effects.

Activated alumina also showed little if any effect of HCl addition.

Table II-8 illustrates these results.

2.2 H_2S Generation

The vapor phase catalytic H_2S generation step was studied over a range of temperatures (600-715°C) and contact times (8-136 seconds) with activated alumina catalyst. High conversions of sulfur ($>$ 85%) and methane ($>$ 90%) to $H_2S + CO_2$ with low COS, CS_2 by-product quantities were achieved at about 10 seconds contact time, 715°C, and excess water.

Near stoichiometric conversions of sulfur and methane to $H_2S + CO_2$ were achieved(as in the pilot plant on 3/19/69):

Contact Time	16 seconds
Temperature	700°C
Molar Feed Ratio ($S/H_2O/CH_4$)	3.8/2.5/1.0 (Stoichiometric = 4/2/1)
% Conversion, CH_4	99%
S	100%
Moles/Mole CH_4 Feed as	
H_2S	4.12 (Theoretical = 4.0)
CO_2	1.00 (theoretical = 1.0)
COS	0.04
CS_2	0.0

Excess water was found to reduce COS + CS_2 formation.

Table II-9 summarizes some of the bench scale results.

With no water in the feed, the following reaction prevails:

$$CH_4 + \frac{4}{X} S_X \longrightarrow CS_2 + 2H_2S \ .$$

High conversions were achieved for this reaction over the alumina catalyst at 675°C, long contact times and stoichiometric feed ratios. Because CS_2 was found to be inactive as an SO_2 reductant, this reaction was not optimized.

3. State of Development

The process technology is considered to be in an advanced state. Catalysts, operating conditions, effects of flue gas composition and maintenance of catalyst activity for the SO_2 reduction are generally well understood. Scale-up and engineering development in a PCR pilot plant were underway at the completion of the NAPCA funded program.

Generation of the H_2S by the novel route was completely successful; near theoretical yields were reached under unoptimized conditions. Scale-up was achieved and pilot plant yields better than bench scale were reached. Incentive for further optimization are small, for the costs of this step are minor relative to the costs of the reduction step.

3.1 Pilot Plant Design, Construction and Operation

A major, integrated, coal burning, continuous pilot plant was designed, constructed, and operated for a short time:

(a) The pilot plant was designed on the following basis:

- 23 SCFM flue gas, 0.2% SO_2
- 8 Pounds per hour pulverized coal, 3% sulfur
- 5 Pounds per day sulfur product

(b) The pilot plant was constructed integrating all the process steps:

- Flue gas generation
- H_2S generation
- SO_2 reduction
- Sulfur recovery

(c) The pilot plant:

- Was constructed of materials believed suitable for commercial use.
- Was instrumented for variation of the process parameters.

(d) Major startup problems were encountered and solved in:

- Feeding small quantities of pulverized coal.
- Design and operation of a pilot scale coal combustion unit.
- Handling sulfur at low flow rates.

3.2 SO_2 Reduction

3.21 Catalysts

The state of catalyst development is considered adequate at this time. Any further work is considered to be improvement studies.

Although three classes of catalysts were found to be useful for SO_2 reduction by H_2S, the activated alumina catalyst was affected severely by the presence of nitrogen oxides in the flue gas.

Molecular sieve 13X was not affected by any of the trace gas compounds studied, but projected prices for the sieves are not as favorable as the alumina. Catalyst development along the lines of modified aluminas may be warranted. Activated bauxites were not studied for an NO_x containing flue gas.

There would appear to be great incentive to development of a catalyst to reduce nitrogen oxides with H_2S.

3.22 Scale-Up

Scale-up of the SO_2 reduction step was inconclusive and requires further work. With the alumina catalyst, the following experimental conditions were run in the pilot plant:

	Source of		Range of	
Flue Gas	H_2S	SO_2	Space Velocity V/V/HR	Temperature °F
Air	H_2S Generator	Gas Bottles	1000-2000	248-257
Combustion of Coal	H_2S Generator	Sulfur in Coal	2300-2900	212-260
Combustion of Coal	Gas Bottles	Sulfur in Coal	2000-2800	212-239
Combustion of Coal	Gas Bottles	Sulfur in Coal	1100-1600	203-275
Combustion of Natural Gas	Gas Bottles	Gas Bottles	1100-2100	176-221
"	" "	" "	1900	212
"	" "	" "	1600	203-230

With the 13X molecular sieve, the following conditions were run:

Combustion of Natural Gas with Bottled NO_x added	Gas Bottles	Gas Bottles	1500	212

All of these experiments either resulted in poor conversions initially or a continuous decline of a high initial conversion. See Table II-10 and Section IV-2.

Several reasons are believed to have possibly contributed to this result:

(a) Insufficient data and operating time

- Severe delays in delivery and start-up of the coal combustor reduced the operating time from a projected seven months to slightly more than two months.
- Most the work was done with activated alumina, later found to be very affected by nitrogen oxides.
- Molecular sieves were tried for only one week, not a long enough period of time to gather meaningful data.
- The catalyst stripping and regeneration system was not studied adequately during operation and may not have been functioning as expected.

(b) Major differences between bench and pilot plant

- Larger catalyst particles were used
- Combustion flue gases were used and certainly contained at least traces of extraneous materials such as fly ash, SO_3, and unburned hydrocarbons which were not studied at the bench.
- Higher linear velocities were used in the pilot plant even though space velocities were the same.

Pilot plant operating data are required for a prototype plant design. Effects of catalyst size, space velocity, temperature, and linear gas velocity must be determined. Sulfur stripping and recovery conditions must be optimized. Catalyst life expectancy must be developed. Pressure drop measurements must be made over a reasonable long time period. Further pilot planting is required.

3.23 Reaction Control

H_2S is an odorous air pollutant, and emissions must be carefully controlled. Laboratory data indicate emissions of H_2S can be limited to about 50 ppm by maintaining the H_2S/SO_2 ratio below 2/1. See Table II-11.

Emissions of 50 ppm result in a maximum ground level concentration below typical H_2S permissible standards. See Section V-1.

Emissions of H_2S at H_2S/SO_2 ratio of 2.3/1 only rise to about 130 ppm. This departure from the stoichiometric excess of 600 ppm is believed due to H_2S oxidation by O_2. See Table II-11.

Pilot plant confirmation of emissions control is required.

A safeguard cleanup system for major upsets may be desirable.

3.24 Reactor Design

The reactor design chosen for the process design must be studied for mechanical feasibility. The large size (>50' diameter) may cause fabrication problems and may not be suitable for the temperature cycling required (250 → 950°F).

Other types of reactors such as fluid beds and moving beds must be considered. Alternate materials of construction should be compared.

The reducing reactor(s) will account for more than two-thirds of the major purchased equipment costs. See Section V-1.

3.25 Materials of Construction

Adequate materials of construction appear to be available for the reducing and sulfur stripping sections. Many of these were utilized in the pilot plant. All were included in the cost estimates of the process:

Flue Gas Fans	Mild Steel
Flue Gas Cooling Chamber	Epoxy Coated Mild Steel
Reducing Reactors	Stainless Steel
Stripping Gas Blower	Epoxy Coated Steel
Stripping Gas Heater	Alloy Tubes
Sulfur Scrubber	Stainless/Mild Steel
Sulfur Pumps and Cooler	Mild Steel

No significant corrosion of these suitable materials was detected in the pilot plant.

3.26 Effects of Flue Gas Composition

Although the effects of the concentration of oxygen, water, sulfur dioxide, nitrogen oxides, chlorides, hydrogen sulfide are believed to be well understood, two areas require further investigation:

(a) Concentrations of SO_2 greater than 0.2-0.3%.

(b) Effects of and/or disposition of carbonyl sulfide, carbon monoxide, methane, sulfur trioxide, carbon disulfide, and fly ash.

Only one other concentration of SO_2 was studied. A 10% SO_2 stream with 1.8% O_2, balance N_2 as in an undiluted smelter gas stream was successfully processed to 95% removal of SO_2. Higher oxygen and water containing streams were not studied.

The effects of and/or disposition of the compounds of (b) must be determined. Study during future pilot planting would be appropriate.

3.3 H_2S Generation

The H_2S generation step is believed to be fully developed including scale-up, reactor design, and materials of construction.

3.31 Catalysts

Activated alumina catalyst was found to perform well in this process. Near theoretical yields were achieved both in bench scale and pilot scale.

Any future catalyst development would be considered as improvement study. Such development would be warranted if the H_2S generation process were to be used for some other purpose, where its cost were a more significant number.

The cost of the H_2S reactor is a small percentage (1%) of the total major purchased equipment costs even with a residence time of 10 seconds.

Catalyst life has not been determined, but again, this is not important to the SO_2 removal process.

3.32 Scale-Up

This step was successfully scaled up in the short pilot program. Better yields were obtained in the pilot plant, although the contact time was somewhat higher. See Table II-12.

3.33 Reactor Design and Materials of Construction

A fixed bed reactor has been found to be technically and economically suitable.

Although the refractory-lined (alumina) steel reactor tested in the pilot plant experienced a rupture, it is believed to be fully resistant to corrosion.

The ruptured reactor was found to have experienced a very severe ($>$2000°F) temperature surge because of loss of control of the electrical heating system used in the pilot plant. Such a temperature rise would not be possible in a commercial reactor because it would be adiabatic with no external heat input.

There was some evidence that stainless steel had a useful life when the temperature control was good, but it is not considered likely that it would be adequate for the reactor shell.

4. Projected Economics

Several important features of the process have economic significance in addition to capital and operating costs:

(a) The process directly produces elemental sulfur by-product.

(b) The process has the thermodynamic potential of reducing NO_x (by reaction with H_2S) in the flue gas concurrently with SO_2.

(c) No solid waste disposal problem is created.

Because of the great volume of sulfur in flue gases relative to the annual consumption of sulfur, the form that the sulfur is recovered in will be of great importance.

Elemental sulfur can be economically stored and shipped, even exported, and, except in limited circumstances, will be preferred over sulfuric acid, sulfur dioxide, hydrogen sulfide, sulfates, sulfites.

Although NO_x reduction by H_2S has not been studied, the thermodynamics are very favorable to this reaction.

Because no absorbent is used and because the catalyst is readily regenerated, no solid waste is produced by the process.

4.1 Process Design

A process design was carried out for a new 1400 Megawatt power plant producing 2.5 million standard cubic feet per minute of 0.3% SO_2 flue gas. A switching fixed bed reactor system for the reduction reaction was chosen. A fixed bed reactor for the H_2S generator was assumed. Sulfur stripping and recovery and catalyst regeneration was based on a closed loop N_2 + H_2S recirculation system. Booster fans for the flue gas and molten sulfur storage were included.

Material balance, flowsheet, major equipment list, and utility requirements may be found in Section V.

The design is based on activated alumina catalyst, which will not function well in the presence of nitrogen oxides. The economics will have to be adjusted as indicated in paragraph 4.3 unless the NO_x is removed or reduced prior to the reactors, or the alumina can be modified to perform in their presence.

4.2 Investment and Operating Costs

For the 1400 Megawatt power plant previously described, a total investment of $11,400,000 ($8.15/KW) is projected. This investment was comprised as follows:

Purchased Equipment	$2.91 MM
Physical Plant Costs (Including offsites)	7.80
Direct Plant Costs (Including engineering and construction)	8.70
Fixed Capital Costs (Including contingency)	9.40
Total Investment (Including interest, working capital and initial catalyst charge)	11.40

Operating costs (before by-product credits) for a 90% operating factor were determined according to the NAPCA guidelines:

Raw Materials	$210,000/year
Utilities	2,128,000
Labor	146,000
Operations	871,000
Capital Charges	1,222,000
Total	$4,577,000

This corresponds to $1.00/ton coal, and would require a netback on sulfur sales of $33/ton sulfur for breakeven.

4.3 Sensitivity of Economics

The economics are particularly sensitive to:

(a) Sulfur content of the coal

(b) Plant size

(c) Operating factor

(d) Catalyst cost

Obviously, the greater items (a), (b), (c) are and the lower (d) is, the better the economics. Figures II-1, 2, 3 are correlations of investments and operating costs with these variables.

Section V-2.4 details some attractive economic circumstances where significant reductions in operating costs may be made.

TABLE II-1

EQUILIBRIUM LIMITATION OF H_2S-SO_2 REACTION AND EFFECTS OF OXYGEN - AT HIGH TEMPERATURE

Gas Composition: 0.2% SO_2, O_2, H_2S, H_2O as below, balance N_2 plus CO_2

Temperature: 392°F. Flow Rate ~1100 std. cc's/min.

Catalyst: Porocel Activated Bauxite (5 gms)

Original Run No.	% O_2	% H_2O	H_2S/SO_2	% SO_2 Conv.	% H_2S Conv.
27	3.7	5.6	2.1	7	16
28	3.8	0.0	2.1	36	80
31	0.0	6.0	2.0	7	14
29	0.0	0.0	4.0	96	49 (98% of theoretical)

TABLE II-2

TYPICAL CONDITIONS FOR HIGH SO_2-H_2S CONVERSIONS

Original	Gas Composition, %						Space	Contact Time,	Temp.,	% Conversions	
Run No.	H_2S	SO_2	N_2	H_2O	O_2	CO_2	Velocity Hr^{-1}	Sec.	°F	H_2S	SO_2
43[a]	0.39	0.18	76.6	5.0	3.5	14.4	$\sim$4000	0.90	257	98.5	98.5
58[a]	0.39	0.21	77.1	5.6	3.7	13.2	2900	1.24	257	98-100	97-100
70[b]	0.4	0.2	75.9	5.0	4.5	14.0	2400	1.50	257	93-95	91-98
72[c]	0.4	0.2	75.9	5.0	4.5	14.5	2700	1.33	257	>95	>95
11A[d]	0.4	0.2	75.9	5.0	4.5	14.0	2700	1.33	257	99.7	98.9
33A[d]	0.4	0.2	75.9	5.0	4.5	14.0	2700	1.33	230	98.0	100.0
39A[d]	0.4	0.2	75.9	5.0	4.5	14.0	2700	1.33	230	100.0	100.0

[a] Spence Activated Alumina (Actal)

[b] Alcoa H-151 (Activated Alumina Gel)

[c] Alcoa F-1 (Activated Alumina Hydrate)

[d] MCB AX-610 (Activated Alumina)

TABLE II-3

TYPICAL RESULTS OF SO_2 REDUCTION IN SMELTER GAS

Catalyst: MCB AX-610 Activated Alumina, 10-14 mesh

Feed Composition: 11.3% SO_2, 22.6% H_2S, 5.7% CO_2, 0.88% O_2, 59.5% N_2

Original Run No.	Temperature °F	Space Velocity V/V/HR	Run Time Minutes	H_2S/SO_2 Ratio	% Conversion	
					H_2S	SO_2
70A	527	4100	200	1.72	87.7	95.5
61A	572	4100	240	2.16	95.0	92.3
64A	662	4100	250	1.98	93.1	84.5
71A	572	1400	360	2.23	95.9	98.2
73A	662	1400	360	1.95	98.5	91.0
76A	752	1400	360	2.70	91.1	97.4

TABLE II-4

CONVERSIONS VS. CATALYST SULFUR LOADING

Original
Run 43

Catalyst: Spence Actal A Activated Alumina, 10-20 mesh, 15 grams

Feed Composition: 0.34% H_2S, 0.18% SO_2, 76.6% N_2, 3.5% O_2, 5.0% H_2O, 14.4% CO_2

Temperature: 257°F

Gas Flow Rate: 1080 cc/min

Run Time	% Sulfur Loading	Conversion	
		% H_2S	% SO_2
2 hrs.	6.1	~ 98	~ 98
4	12.1	~ 98	~ 98
8	24.3	~ 98	~ 98
10	30.4	~ 70	~ 95
16	--	--	~ 65

NOTE: This data not reported elsewhere in the report.

TABLE II-5

CATALYST DEACTIVATION DURING SULFUR STRIPPING WITH N_2

Catalyst: Spence Actal

Temperature: 257°F

Space Velocity: ~4000 Hr^{-1}

Gas Composition: 0.4% H_2S, 0.2% SO_2, 76.5% N_2, 5% H_2O, 3.5% O_2, 14.3% CO_2

Sulfur Stripping: Raise catalyst bed to >450°C with N_2 flow across it.

Original Run No.	Conversion	% H_2S	% SO_2
43	Initial	98.5	98.5
44	Second Cycle	97.0	98.0
45	Third Cycle	92.2	91.4

TABLE II-6

RESTORATION OF CATALYST ACTIVITY BY CONTACT WITH H_2S AT HIGH TEMPERATURE

Original Run No.	42A	43A	44A	45A	46A	47A	48A
Catalyst History	Run 41A	Run 42A	Run 43A	Run 44A	Run 45A	Run 46A	Run 47A
SO_2 Reduction[(1)]							
Length of Run, min.	302	355	215	410	315	270	235
Average Conversion (2)							
% H_2S	71.2	100.0	84.0	95.2	97.9	93.1	98.2
% SO_2	73.3	100.0	86.0	98.5	96.4	74.8	100.0
Sulfur Stripping							
Treatment Before Stripping	None ——————→						
Stripping Conditions							
Gas	N_2	N_2	N_2	N_2	N_2	5% H_2S+ 95% N_2	5% H_2S+ 95% N_2
Rate, ml/min.	300	300	300	300	300	52	53
Temperature, °F[(3)]	230-662	230-662	230-662	230-662	230-662	230-932	230-932
Period, min.	120	120	155	82	175	177	170
Treatment After Stripping							
Gas	H_2S	N_2	0.5% H_2S, 99.5% N_2	10% H_2S, 90% N_2	2% H_2S, 98% N_2	None	None
Rate, ml/min.	50	50	660	55	51		
Temperature, °F	932	932	932	932	932		
Period, min.	120	120	120	150	122		

Notes:

(1) Catalyst: 67 gms, 70 mls MCB AX-610 Activated Alumina
Temperature: 230°F Feed Rate: 3060 ml/min. Space Velocity: 2700 hr^{-1}
Gas Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14.0% CO_2, 5.0% H_2O.

(2) Average conversion during 6 hours of run, or during entire run if run <6 hours.

(3) Reactor rapidly heated to upper temperature of range indicated, then held at upper temperature.

TABLE II-7

CATALYSTS FOUND EFFECTIVE FOR SO_2-H_2S REACTION

Temperature:	257°F
Space Velocity:	2700 Hr^{-1} (1.33 seconds contact time)
Gas Composition:	0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14.0% CO_2, 5.0% H_2O

ILLUSTRATIVE DATA

Original Run No.	Catalyst	Average 6 Hr. Activity % H_2S Conv.	Average 6 Hr. Activity % SO_2 Conv.
11A	MCB AX-610 Activated Alumina (Reynolds RA-3)	99.7	98.9
73B	Linde 13X Molecular Sieve	98.0	99.3
79B	Porocel Sulfur Recovery Catalyst (Granular Activated Bauxite)	91.9	100.0

TABLE II-8

EFFECTS OF NITROGEN OXIDES ON H_2S AND SO_2 CONVERSIONS

ACTIVATED ALUMINA CATALYST, 10-20 MESH

Original Run No.	Nitrogen Oxide Addition, ppm NO	Nitrogen Oxide Addition, ppm NO_2	Average Measured Feed Ratio, H_2S/SO_2	Time of Run, min.		% Conversion H_2S	% Conversion SO_2
83A	450	50	1.82	14		100.	100.
				72		100.	100.
				159		71.3	60.8
				244		83.5	65.9
				274		83.2	69.2
					Avg.	87.6	79.2
84A-1	0	0	2.06	3		100.	100.
				36		100.	100.
				100		100.	
					Avg.	100.	100.
84A-2	500	0	2.06	4		100.	100.
				80		87.5	76.6
				143		68.9	76.6
				230		65.5	56.6
					Avg.	80.5	77.4

13X MOLECULAR SIEVE CATALYST, 10-20 MESH

Original Run No.	Nitrogen Oxide Addition, ppm NO	Nitrogen Oxide Addition, ppm NO_2	Average Measured Feed Ratio, H_2S/SO_2	Time of Run, min.		% Conversion H_2S	% Conversion SO_2
92A	450	50	2.13	34		86.6	100.
				69		95.9	100.
				192		94.6	100.
				252		92.6	100.
					Avg.	92.4	100.

Runs 89A-91A show similar results for the molecular sieve catalyst, but the large particle size (4-8 mesh) used in those runs apparently caused channeling in the small, low velocity bench reactor. Average H_2S conversions were 84-88%. Average SO_2 conversions were 96-99%.

Temperature in all runs was 230°F. Space velocity in all runs was 2700 Hr^{-1}.

TABLE II-9

H_2S GENERATION DATA

Original Run No.	Superficial C.T. Seconds	Temp., °F	$H_2O/^{(a)}$ CH_4	$S_2/^{(a)}$ CH_4	% Conversions, CH_4	% Conversions, S	Moles Product / $CH_4^{(b)}$ H_2S	Moles Product / $CH_4^{(b)}$ CO_2	Moles Product / $CH_4^{(b)}$ COS	Moles Product / $CH_4^{(b)}$ CS_2
		CATALYST: 8-9 Mesh Matheson Activated Alumina								
26	11	1242	2.06	1.92	83.2	80.0	3.18	0.64	0.09	0.01
27	11	1319	2.14	1.98	97.5	94.0	3.26	0.29	0.43	0.07
28	11	1274	2.06	1.91	92.8	90.4	3.51	0.49	0.18	0.01
29	8	1276	3.95	1.91	82.7	73.9	3.00	0.70	0.02	0.00
30	8	1319	4.19	2.04	90.7	--	3.43	0.76	0.01	0.00
31	8	1319	4.32	2.06	92.6	89.6	3.61	0.82	0.03	0.00
32	9	1319	3.54	2.07	94.0	85.2	3.71	0.80	0.02	0.00
33	10	1319	2.70	2.07	97.4	90.2	3.68	0.76	0.05	0.00
34	11	1319	2.14	2.07	98.3	83.5	3.53	0.70	0.08	0.00
		CATALYST: Spence Activated Alumina 10A, 8-9 Mesh								
36	11	1319	2.16	2.07	98.4	92.4	3.76	0.71	0.14	0.00
37	9	1319	3.69	2.35	94.6	91.0	3.77	0.77	0.04	0.00

(a) Stoichiometric $H_2O/CH_4 = 2.0$
$S_2/CH_4 = 2.0$

(b) Theoretical $H_2S/CH_4 = 4.0$
$CO_2/CH_4 = 1.0$
$COS, CS_2 = 0.0$

TABLE II-10

TYPICAL COMPARISON OF PILOT PLANT AND LAB DATA

SO_2 Reduction$^+$

	Pilot Plant(6/5-6/11)		Bench Scale Original Run 84A-2	
Flue Gas:	Pulverized coal		Bottled gases	
NO_x Content:	Estimated @ 10-50 ppm		500 ppm	
Hours On	Conversion		Conversion	
Stream(Approx.)	H_2S %	SO_2 %	H_2S %	SO_2 %
0	--	99	100	100
1			87	77
2	53	85	69	77
3	93	89	65	57
4				
5				
6				
7	80	64		
8				
9	73	64		
Catalyst:	+3 Mesh		-10 + 20 Mesh	

+ 212-230°F, Contact Time ∿2 seconds

- Activated Alumina Catalyst

TABLE II-11

H_2S EMISSION CONTROL DATA

Catalyst: MCB's AX-610 Activated Alumina

Temperature: 230°F Space Velocity: 2700 Std.Vol./Vol./Hr.

Original Run No.	Time of Run, Min.	Measured Feed Ratio, H_2S/SO_2	Time of Run, Min.	H_2S Exit Concentration, ppm.
98B	35	2.14	211	92
	95	2.05	302	56
	130	2.14	361	135
	180	2.09		Avg. 95
	220	2.10		
	330	2.20		
		Avg. 2.12		
99B	40	1.84	60	76
	72	1.76	120	47
	110	1.88	180	50
	140	1.89		Avg. 58
	180	1.85		
		Avg. 1.84		
100B	45	2.10	60	82
	90	2.04	90	80
	120	2.06	120	69
	135	2.09	180	68
	240	2.04	240	55
		Avg. 2.06		Avg. 71
101B	115	2.05	120	64
	180	1.72	180	50
	300	1.78	240	39
	330	1.79	300	35
	360	1.74	360	38
		Avg. 1.82		Avg. 45
102B	60	2.48	120	142
	125	2.30	180	127
	180	2.25	240	124
	240	2.28	300	122
	300	2.28		Avg. 128
		Avg. 2.32		
103B	60	2.84	120	259
	120	2.86	180	225
	180	2.84	240	237
	240	2.84	300	177
	300	2.93	360	237
	360	2.92		Avg. 227
		Avg. 2.87		
104B	60	2.10	120	59
	100	1.86	180	61
	120	1.97	240	60
	180	2.03	300	47
	240	1.97		Avg. 57
	260	1.84		
	300	1.83		
		Avg. 1.94		

TABLE II-12

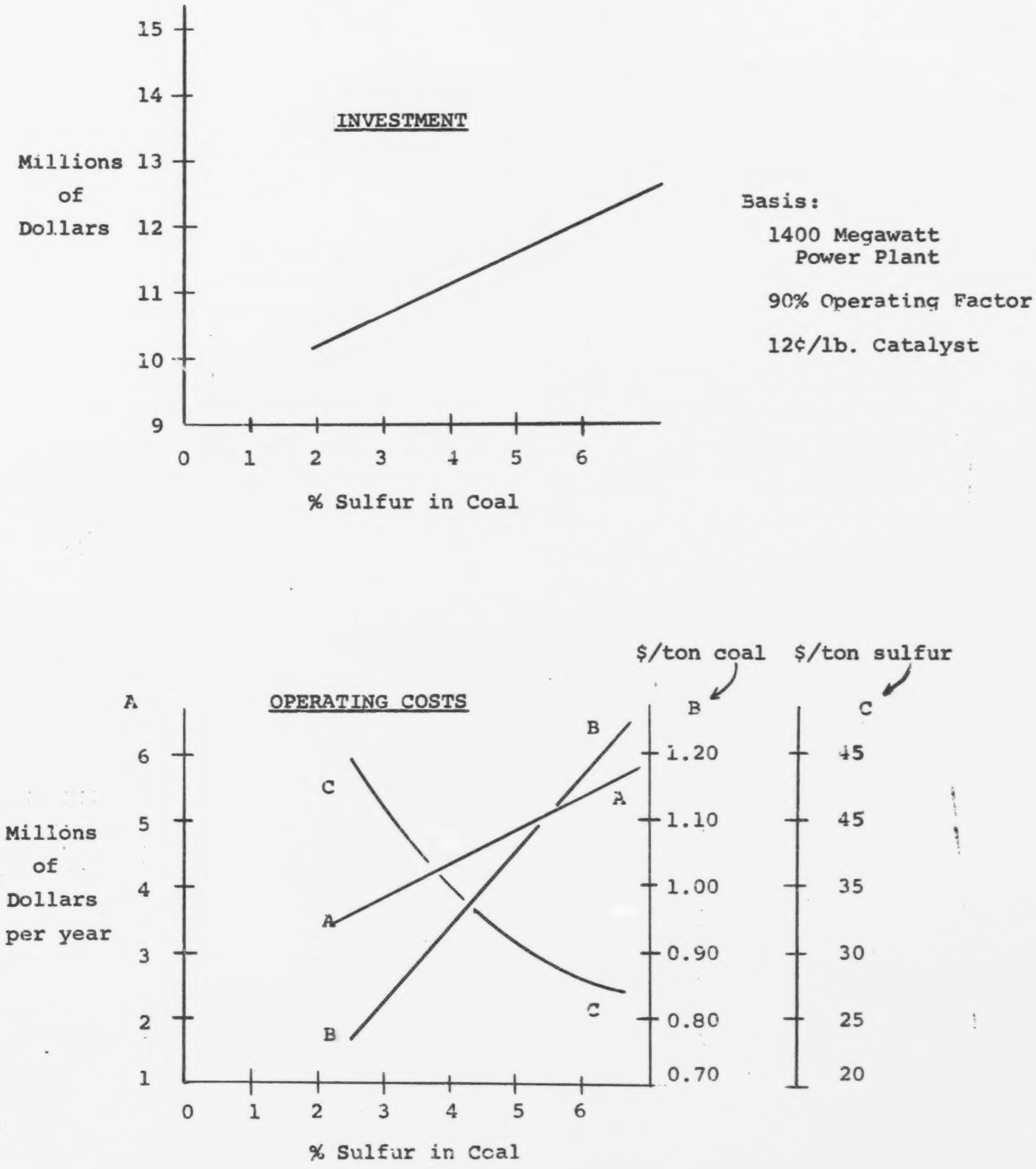
TYPICAL COMPARISON OF PILOT PLANT AND LAB DATA

H_2S Generation

	Pilot Plant (3/19/69)	Bench Scale Original Run 34
Superficial Contact Time, seconds	16	11
Temperature, °F	1292	1319
Feed Ratios $S/H_2O/CH_4$, gm. atoms/gm.mole/gm.mole	3.8/2.5/1.0	4.1/2.1/1.0
% Conversion:		
CH_4	99	98
S	100	84
Moles per mole CH_4 feed as:		
H_2S	4.12	3.53
CO_2	1.00	0.70
COS	0.04	0.08
CS_2	0	0
% of feed accounted for:		
C	100	80
H	-	87
S	100^+	100
O	95	85

FIGURE II-1

ECONOMIC EFFECTS OF SULFUR CONTENT OF COAL



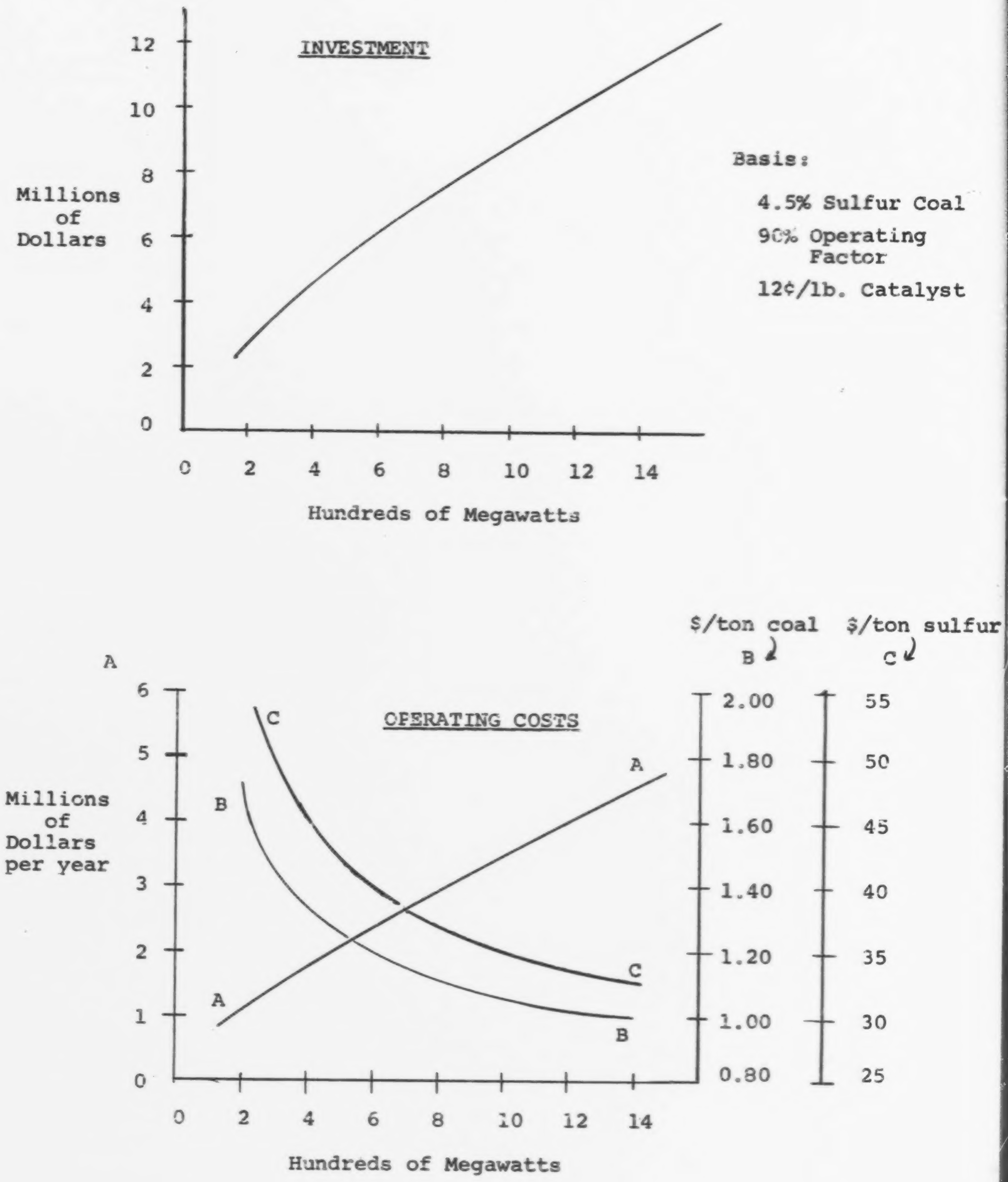
Basis:

1400 Megawatt Power Plant

90% Operating Factor

12¢/lb. Catalyst

FIGURE II-2
ECONOMIC EFFECTS OF POWER PLANT SIZE



Basis:

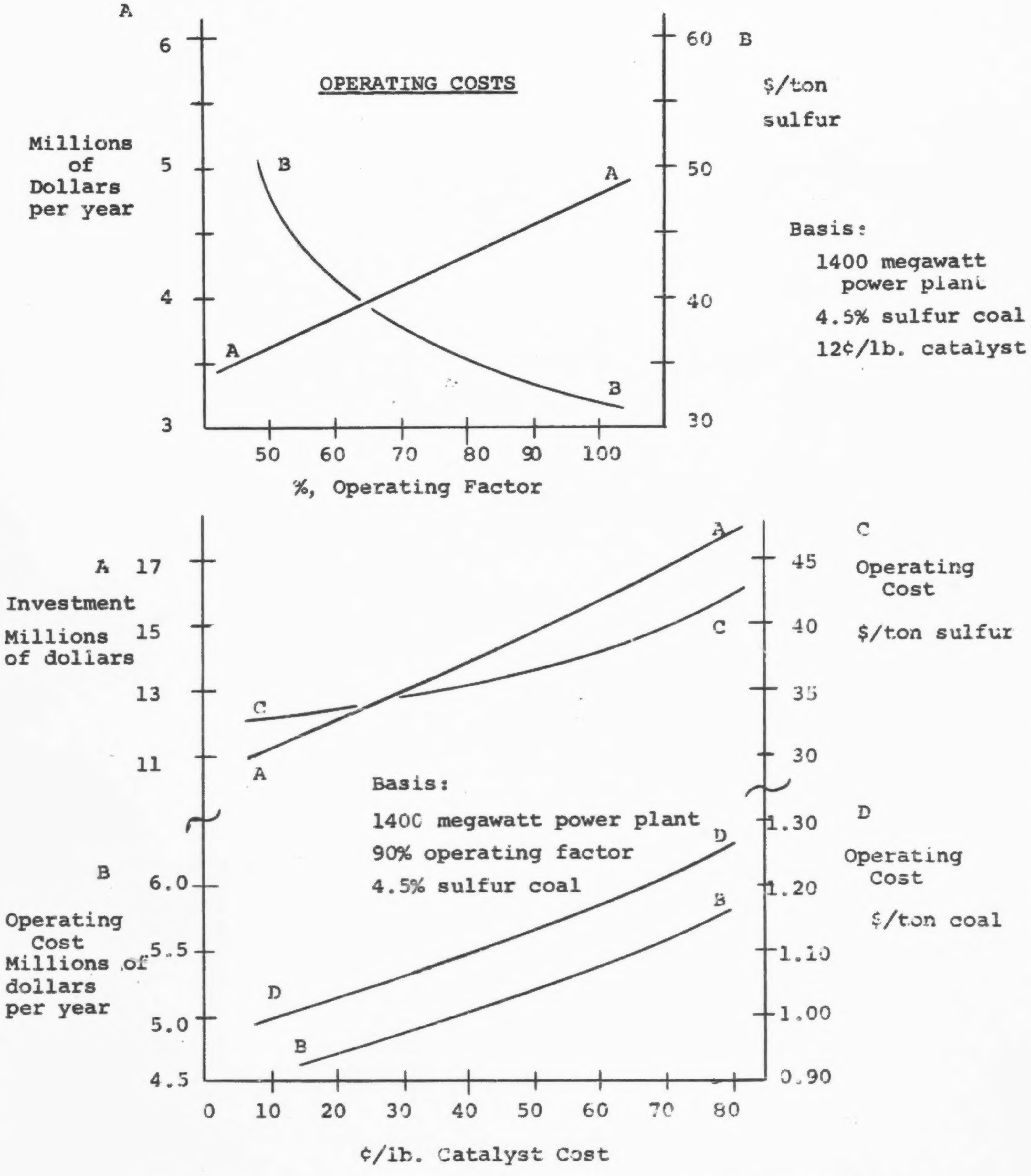
4.5% Sulfur Coal

90% Operating Factor

12¢/lb. Catalyst

FIGURE II-3

ECONOMIC EFFECTS OF OPERATING FACTOR AND CATALYST COST



(Five calendar years, 2.5 onstream years catalyst life)

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION III

LABORATORY

TABLE OF CONTENTS

SECTION III - LABORATORY

Page

1. Experimental Data 49

  1.1 Reduction of Sulfur Dioxide 49

    1.11 Power Plant Flue Gas Concentrations of SO_2 50
    1.12 Smelter Gas Compositions 59

  1.2 Production of Hydrogen Sulfide 60

    1.21 Uncatalyzed Liquid Phase Reaction 60
    1.22 Uncatalyzed Vapor Phase Reaction 61
    1.23 Catalyzed Vapor Phase Reaction 61

2. Experimental Methods 63

  2.1 Apparatus 63

    2.11 Reduction of Sulfur Dioxide 63
    2.12 Production of Hydrogen Sulfide 65

LIST OF TABLES

SECTION III - LABORATORY

Table	Title	Page
III-1	Reduction of Sulfur Dioxide at Power Plant Flue Gas Concentrations: Catalyst Screening	66
III-2	Catalyst Screening Results, Low Temperature SO_2 Reduction	76
III-3	Catalyst Reactivation Studies	77
III-4	Effects of NO_x and HCl on the Catalytic Reduction of SO_2, Activated Alumina Catalyst	84
III-5	Effects of NO_x and HCl on the Catalytic Reduction of SO_2, Molecular Sieve 13X - Type Catalyst	87
III-6	H_2S Emission Control	92
III-7	Reduction of Sulfur Dioxide by Hydrogen Sulfide in a Simulated Smelter Gas Composition	94
III-8	Generation of Hydrogen Sulfide: Uncatalyzed Vapor Phase Reaction of Methane and Sulfur	95
III-9	Generation of Hydrogen Sulfide: Catalyzed Vapor Phase Reaction of Methane and Sulfur	96

LIST OF FIGURES

SECTION III - LABORATORY

Figure	Title	Page
III-1	H_2S Conversion Vs. Time	98
III-2	Activated Alumina Catalyst, Deactivation by NO_x	99
III-3	Effect of Interrupting NO_x Addition, on SO_2 Reduction	100
III-4	H_2S Emission Control	101
III-5	Run R76: H_2S Conversion Vs. Time	102
III-6	Sulfur Dioxide Reduction Assembly No. 1	103
III-7	Sulfur Dioxide Reduction Assembly No. 2	104
III-8	Laboratory Hydrogen Sulfide Generation Assembly	105

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION III - LABORATORY

1. Experimental Data

1.1 Reduction of Sulfur Dioxide

PCR has conducted a laboratory investigation of the reduction of sulfur dioxide to sulfur, via the heterogeneously-catalyzed vapor phase reaction

$$2H_2S + SO_2 \xrightarrow{\text{cat.}} 2H_2O + \frac{3}{X} S_X \ .$$

The majority of the experiments were conducted feeding SO_2 concentrations present in power plant flue gases: 0.2 to 0.3%. A few of the reduction experiments fed SO_2-N_2 mixtures, but most of the work employed simulated flue gas mixtures prepared by blending carbon dioxide, oxygen, nitrogen, water, and sulfur dioxide. In several experiments nitrogen dioxide, nitric oxide, and hydrogen chloride were added to the gas mixtures in attempts to simulate the effects of some of the minor flue gas components.

The reduction of sulfur dioxide by hydrogen sulfide was also demonstrated for a higher SO_2 concentration, 16%, in a simulated smelter gas stream. This stream contained small smounts of oxygen in addition to the sulfur dioxide; the remainder was nitrogen.

The SO_2 reduction reaction was studied over two temperature ranges. In the higher range, i.e., above 200 to 250°C, the vapor pressure of sulfur is high enough that the sulfur produced during the reaction does not deposit continuously on the catalyst surface. Thus, the sulfur may be recovered by condensing it downstream from the catalyst bed.

At temperatures below 200 to 250°C, the sulfur formed continues to deposit on the catalyst, eventually causing the catalyst's activity to fall off. At the lower temperatures, therefore, the reaction was conducted by periodically heating the catalyst to recover the sulfur and re-expose fresh catalyst surface.

A variety of catalysts were examined for suitability for the low temperature SO_2 reduction reaction. The catalysts included activated aluminas, activated carbons, molecular sieves, silica gels, silica-aluminas, and activated bauxites. Most of the catalyst compositions were commercial preparations, but some specially prepared catalysts were also examined.

The catalysts were evaluated for initial activity for SO_2 reduction; if active, they were also examined for regenerability after an intial SO_2 reduction cycle. The most promising catalysts were further evaluated for resistance to deactivation by nitrogen oxides or chloride, which are normally present in power plant flue gases.

In a very limited study, carbon disulfide was evaluated as a possible replacement for hydrogen sulfide as the reductant for SO_2; the CS_2 was found to be unreactive.

1.11 Power Plant Flue Gas Concentrations of SO_2

1.111 Catalyst Screening Experiments

Table III-1 gives a complete tabulation of the runs in which various catalysts were screened for the H_2S-SO_2 reaction at low concentrations of SO_2, nominally 0.2 mole percent.

1.1111 Temperatures Above About 200°C

At temperatures above about 200°C at which sulfur does not continually deposit on the catalyst, and in the absence of oxygen, the reaction conditions are similar to those of a conventional Claus process, except for the present lower concentrations of H_2S and SO_2. Both of the two catalysts evaluated under these conditions, at a space velocity of 3750 hr^{-1}, showed good activity: molecular sieve 4-A (Run R2) and 13X (Runs R57 through R63). The observed H_2S and SO_2 conversions were close to the theoretical equilibrium values, e.g., 92% H_2S conversion at 250°C.(1)

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(1) Munro and Masdin, Brit. Chem. Eng., Vol. 12, No. 3 (March, 1967), p. 370.

Molecular sieve 13X was also active at a space velocity of 7450 hr^{-1}, at temperatures up to 412°C (Runs R67 through R71). At a lower space velocity, 600 hr^{-1}, an empty reactor tube (Run R1) gave evidence of only a very slight reaction at 250°C.

When oxygen, water, and carbon dioxide were added to the simulated flue gas mixture, none of the catalysts evaluated exhibited good H_2S or SO_2 conversions at temperatures above 200°C. The previously active molecular sieve 13X deactivated rapidly: see Runs R67 through R74. A fresh charge of activated bauxite (Runs R21, R22, R23), and MCB's activated alumina (Runs R35, R36) similarly gave poor H_2S and SO_2 conversions, generally below 50%.

Water shifts the equilibrium conversion for the reaction

$$2H_2S + SO_2 \rightleftarrows \frac{3}{X} S_X + 2H_2O$$

unfavorably. However, the reduction in equilibrium conversion due to the addition of 5-6% H_2O is not sufficient to account for the very large differences observed between, say, Run R68 and R73; see Reference (1).

On the other hand, the presence of oxygen in the simulated flue gas composition provides an opportunity for side reactions such as the oxidation of SO_2 or H_2S:

$$2SO_2 + O_2 \longrightarrow 2SO_3,$$

$$\underline{\text{or}}\ 2SO_2 + 2H_2O + O_2 \longrightarrow 2H_2SO_4;$$

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S,$$

$$2H_2S + 2O_2 \longrightarrow 2H_2O + 2SO_2,$$

$$H_2S + 2O_2 \longrightarrow H_2SO_4.$$

Such side reactions may preferentially consume either H_2S or SO_2; or a side product such as sulfate can conceivably poison the catalyst for the H_2S-SO_2 reaction.

With increasing temperature, oxidations by molecular oxygen are expected to become more likely or extensive. Thus, the poor conversions observed in the presence of oxygen and water are more likely related to side reactions involving oxygen, rather than to the effect of water on the equilibrium of the H_2S-SO_2 reaction.

1.1112 Temperatures Below About 200°C

At temperatures below 200°C, and preferably below about 150°C, the sulfur formed continually deposits on the catalyst surface either due to condensation to bulk phase sulfur, or to sorption. In the second case, the vapor pressure of the sorbed sulfur is necessarily lower than that of bulk phase sulfur. The equilibrium conversion for the reaction

$$2H_2S + SO_2 \rightleftarrows \frac{3}{x} S_x + 2H_2O$$

is therefore more favorable than when the sulfur condenses without sorption. It should also be noted that when sulfur sorption occurs, the theoretical equilibrium conversions can not be calculated without a knowledge of the lower sulfur vapor pressure, or its thermodynamic equivalent.

Thus, three factors can contribute to facilitating SO_2 reduction at lower temperatures: the effect of temperature on the equilibrium, the effect of sulfur sorption on the equilibrium, and the reduced likelihood of interference from side reactions involving oxygen.

Table III-2 summarizes the results of the catalyst screening study for the lower temperature SO_2 reductions. Because the runs were not conducted under exactly the same conditions, i.e., somewhat different space velocities, temperatures, and feed compositions were used, only a qualitative comparison of catalyst performance is possible. Another factor which quantitatively affected the apparent catalyst performance was its pellet size; catalysts larger than 10-20 mesh apparently exhibited reduced performance due to some channelling through the bed.* See Runs R80, R81, and R82, in which pellet size was systematically varied.

The outstanding catalysts were found to be molecular sieve type 13X; high surface are aluminas; and activated bauxites. Under optimum conditions with feeds containing 0.2% SO_2, 0.4% H_2S, O_2, H_2O, CO_2, and N_2, all of these catalysts are believed to be capable of giving conversions of H_2S and SO_2 both over 99%, up to sulfur loadings of 20 to 25% based on weight of catalyst.

Catalysts found to be poor or inactive were molecular sieves 3A, 4A, and 5A; rare-earth and hydrogen-exchanged zeolites; silica gels; silica-aluminas; and various modified silica gels.

1.112 Catalyst Reactivation Studies

In the low temperature SO_2 reductions, the best catalysts were found to sustain their initial activity until about 20-25% of sulfur had deposited on them. A rapid decrease in H_2S and SO_2 conversions then followed; see for example, Figure III-1.

The sulfur could then be removed by heating the catalyst in a purge stream of inert gas, to temperatures at which the sulfur would desorb and vaporize, generally 275 to 500°C. However, it soon became apparent that, depending on its previous history, the catalyst did not fully recover its activity for the subsequent sulfur dioxide reduction cycle. See for example Runs

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* The SO_2 reductions were generally run in a 1 in. i.d. tubular reactor containing a 0.25 in. diameter thermowell. This provided an annular space 0.375 in. thick for packing the catalyst. Only pellet sizes smaller than about 14 mesh (i.e., 1/5 of 0.375 in.) are expected to eliminate channelling completely.

R108, R109, R110, R124, R125, R126, in Table III-3; this Table contains all of experimental data for the catalyst reactivation studies.

Various modifications of the sulfur stripping procedure, and other catalyst treatments, were tried in attempts to recover the full activity of two representative activated alumina catalysts, Spence Actal A and MCB's AX-610. These treatments included:

stripping in N_2 at temperatures up to 600°C for periods up to 12 hours (Runs R85 through R89, R54, R55, R91, R92);

stripping in 25% H_2O, 75% N_2 mixtures (Runs R98 through R101);

stripping in N_2 followed by hydration in 5% H_2O, 95% N_2 at 125° (Run R102);

stripping in N_2 followed by treatment with air at 525 to 650°C (Runs R103, R105, R115);

stripping in N_2 followed by washing the catalyst with water (Run R111);

purging the catalyst in dry air at 25°C just prior to stripping (Run R118);

purging the catalyst in 5% H_2O, 95% N_2 at 25°C just prior to stripping (Run R121);

purging the catalyst in N_2 at 25° or 125°C just prior to stripping (Runs R122, R128).

At best, any of the above procedures only resulted in partial, but not full reactivation of the catalyst.

Significantly, however, the water washing treatment resulted in a substantial recovery in catalyst activity: H_2S conversion increased from below 50% in Run R110 to 94% in R111. This suggested that the catalyst deactivation may have been related to the presence of some water-soluble species on the catalyst surface after stripping. Qualitative tests indicated the presence of sulfate ion in the water-extract of a stripped, deactivated alumina catalyst; while the same catalyst fresh contained small traces of extractable sulfate or none at all.

In Runs R139 through R156, hydrogen sulfide was introduced during or after sulfur stripping cycles in order to remove possible traces of sulfate on the catalyst by reduction; for example, by a reaction such as

$$3H_2S + H_2SO_4 \longrightarrow 4H_2O + 4S$$

The result was dramatic. Exposing the catalyst to H_2S or H_2S-N_2 mixtures containing at least 5% H_2S, at temperatures of 500°C, resulted in complete reactivation. This reactivation procedure was most conveniently accomplished in the laboratory by stripping the catalyst in a 10% H_2S - 90% N_2 mixture at temperatures from 110° to 500°C, and then maintaining the catalyst at 500°C in the H_2S-containing atmosphere for 2 hours. This combined the sulfur stripping, and reactivation processes into a single treatment.

1.113 Effects of NO_x and HCl

1.1131 Activated Alumina Catalyst

Table III- 4 gives the results of experiments in which nitrogen oxides and hydrogen chloride were added to the simulated flue gas composition, for SO_2 reduction over a typical activated alumina catalyst (MCB AX-610).

In Runs R157 to R159, attempts were made to introduce nitrogen oxides by feeding nitric acid at a rate corresponding to 500 ppm, and pyrolyzing the acid at 250°C just before mixing with the simulated flue gas stream. No attempts were made to measure the extent of nitrogen oxide formation, but this method of addition had little effect on H_2S or SO_2 conversions.

In Runs R161 and R162, 500 ppm of hydrogen chloride was added to the simulated flue gas mixture. This concentration of HCl is probably several times higher than would be encountered in a real power-plant flue gas. The result was little, if any, effect on H_2S or SO_2 conversions.

In other experiments, 500 ppm NO_x was added to the simulated flue gas mixture, either as 100% NO, 100% NO_2, or as 90% NO + 10% NO_2. The last mixture is believed to be a typical NO_x concentration and composition in a real power-plant flue gas.

The effects of 500 ppm NO_x on the reduction of SO_2 are plotted in Figure III- 2 for MCB activated alumina. From this plot it is apparent that

(i) 500 ppm NO_x causes rapid and severe deactivation of an activated alumina catalyst during the SO_2 reduction cycle;

(ii) it is immaterial whether NO_x is introduced as NO, NO_2, or a NO-NO_2 mixture; and

(iii) H_2S conversion decreases somewhat less rapidly than SO_2 conversion. From the data in Table III- 4, it is also evident that when deactivation has occurred, the catalyst is fully regenerated when stripped in a H_2S-N_2 mixture.

After one run, R166, the addition of NO was discontinued, and SO_2 reduction was continued (as Run R167) without any other interruptions. The results are plotted in Figure III-3. The partial recovery of catalyst activity after stopping the NO_x addition suggests that the deactivation may be due to the poisoning of active sites by a reversible adsorption of NO_x molecules. The final fall-off of H_2S and SO_2 conversions in Run R167 was probably caused at least partly by sulfur deposition.

The results of Run R168 indicate that a relatively low concentration of NO_x, viz. 50 ppm as NO_2, has little or no effect on catalyst activity.

1.1132 Molecular Sieve 13X Catalyst

Table III-5 contains the results of experiments which demonstrate the effects of nitrogen oxides and hydrogen chloride on Linde Molecular Sieve 13X catalyst. In Runs R179 through R173, R75, R76, and R174 through R177, NO_x was added as 50 ppm NO_2 + 450 ppm NO. This catalyst was completely resistant to deactivation by NO_x during SO_2 reduction, and also maintained its excellent activity through several SO_2 reduction and sulfur stripping cycles.

In Runs R178 and R179, 100 ppm HCl was added in addition to the 500 ppm NO_x. Again, the catalyst exhibited excellent sustained activity.

Runs R80 through R84, Table III- 5 , demonstrate that a second molecular sieve 13X type catalyst, Davison 542, was also resistant to deactivation by nitrogen oxides.

1.114 Effects of H_2S/SO_2 Feed Ratio

Table III-6 lists a series of runs in which the H_2S/SO_2 feed ratio was systematically varied in a simulated flue gas composition containing SO_2, CO_2, O_2, H_2O, and N_2. The catalyst was MCB AX-610 Activated Alumina.

The average ppm H_2S in the tail gas from the SO_2 reductor is plotted in Figure III-4 against the average measured H_2S/SO_2 feed ratio for each run. The "theoretical" comparison curve in this graph assumes that the only reaction by which both H_2S and SO_2 disappear is $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$, and that this reaction proceeds to stoichiometric completion.

The curve clearly indicates that residual H_2S levels for this catalyst are surprisingly insensitive to H_2S/SO_2 ratios. For example, at 40% excess H_2S (ratio 2.8), residual H_2S is only 14% of "theoretical". At 10% deficient H_2S (ratio 1.8), residual H_2S is $\sim$45 ppm, while "theoretical" is of course zero. At H_2S/SO_2 = 2, residual H_2S was $\sim$70 ppm.

At less than stoichiometric H_2S/SO_2 ratios, the finite residual H_2S level may be due to:

(i) the equilibrium conversion* of H_2S being less than, say, 98.5%;

or (ii) the equilibrium conversion of H_2S being prevented by kinetic limitations.

At high H_2S/SO_2 feed ratios, the excess of H_2S (over the stoichiometric requirement by SO_2) probably disappears largely by the oxidation of H_2S by molecular oxygen, either to sulfur or to sulfate.

Figure III- 5 plots measured H_2S against run time for Run R76 (Table III-1). The curve for "theoretical" H_2S conversion is plotted for comparison. The points on the theoretical curve are H_2S conversions calculated from measured H_2S/SO_2 feed ratios, assuming that the unconverted H_2S is the excess of H_2S over that required for stoichiometric completion of the reaction $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$, similar to the "theoretical" conversions used for calculating residual H_2S in Figure III-4

The measured H_2S conversions follow the theoretical curve fairly well. This suggests that unlike the activated alumina case, the stoichiometric excess of H_2S is probably not readily converted by oxidation to sulfur or sulfate, and thus largely shows up in the tail gas.

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*Since the sulfur adsorbed on the catalyst undoubtedly has a lower vapor pressure than bulk phase sulfur, the equilibrium conversion for the reaction $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$ (adsorbed) is necessarily greater than that calculated by assuming that the sulfur has its bulk phase vapor pressure.

1.115 Use of CS_2 as a Reductant

In two experiments attempts were made to replace H_2S by CS_2, as the reductant for sulfur dioxide at power plant flue gas concentrations:

$$CS_2 + SO_2 \longrightarrow CO_2 + \frac{3}{X} S_X$$

Compositions containing 0.2% CS_2, 0.2% SO_2 and 99.6% N_2 were fed over Engelhard Porocel activated bauxite, and Spence Actal activated alumina, respectively, at 200°C, and space velocities of 12,000 std.vol./vol. of catalyst bed/hr.

No reaction took place.

1.12 Smelter Gas Compositions

A series of experiments was conducted to demonstrate the feasibility of reducing SO_2 to sulfur in an undiluted smelter gas composition, consisting of 15.8% SO_2, 1.2% O_2, and 83.0% N_2. The reductant was an 80% H_2S-20% CO_2 mixture, such as obtained by the reaction of methane, water, and sulfur:

$$CH_4 + 2H_2O + \frac{4}{X} S_X \longrightarrow CO_2 + 4H_2S.$$

The catalyst was a typical activated alumina, MCB AX-610. The experimental data for these runs is contained in Table III-7.

The reductions were conducted at 250° to 400°C, so that sulfur did not continually deposit on the catalyst, but was condensed downstream from the reactor. Space velocities were 4100, and 1400 std.vol./vol. of catalyst bed/hr. At H_2S/SO_2 feed ratios near 2, sustained conversions of about 95% each for H_2S and SO_2 were obtained at an optimum temperature of about 350°C.

This series of experiments leads to the following conclusions:

(i) H_2S and SO_2 conversions are not very sensitive to space velocity (i.e., to contact time) in the range 1400 to 4100 std.vol./vol./hr., i.e., they are probably close to equilibrium conversions.

(ii) Observed H_2S and SO_2 conversions do not vary much with temperature in the range 250-350°C.

(iii) The conversions are quite sensitive to the feed ratio of H_2S/SO_2, the conversion decreasing for whichever component is in excess of the stoichiometric ratio. For $H_2S/SO_2 = 2$, conversions are typically both about 95%.

(iv) No catalyst deactivation is observed after up to ~60 hours of intermittent operation on a single charge of activated alumina catalyst.

1.2 Production of Hydrogen Sulfide

PCR has conducted a laboratory study of a process for the production of hydrogen sulfide by the reaction of methane and sulfur. The hydrogen sulfide thus produced is intended as the reductant for sulfur dioxide.

The uncatalyzed reactions of methane and sulfur were examined briefly both in the liquid and vapor phase. However, the majority of the experiments employed activated alumina as a catalyst. Most of the catalytic experiments incorporated water as a co-reactant:

$CH_4 + \frac{4}{X} S_X + 2H_2O \longrightarrow CO_2 + 4H_2S$, in order to suppress the formation of carbon disulfide which forms in the absence of water:

$$CH_4 + \frac{4}{X} S_X \longrightarrow CS_2 + 2H_2S.$$

1.21 Uncatalyzed Liquid Phase Reaction

A few exploratory experiments were conducted in which methane was bubbled through molten sulfur at temperatures up to 400°C. Minor amounts of hydrogen sulfide were found in the effluent, and methane conversions were estimated at less than 0.5%.

Because of the poor reactivity under these conditions, the liquid phase experiments were not pursued.

1.22 Uncatalyzed Vapor Phase Reaction

Data for the two uncatalyzed vapor phase runs are given in Table III-8. In these experiments, mixtures of sulfur vapor and methane were conducted over a bed of rock-salt, which has been previously reported to be non-catalytic(2) for the methane-sulfur reaction. At 607°C, feeding 3.8 g-atom S/g-mole CH_4 at 13.6 hr^{-1} space velocity, resulted in 36% conversion of methane, with 66 and 29 mole % yields* of H_2S and CS_2, respectively.

$$^* \text{ Mole \% Yield} = \frac{\text{mole of product}}{\text{mole of } CH_4 \text{ converted}} \times 100\%.$$

For the reaction $CH_4 + \frac{4}{X} S_X \longrightarrow 2H_2S + CS_2$, when a stoichiometric ratio of methane to sulfur is fed, theoretical yields are 200 and 100 mole % for H_2S and CS_2, respectively.)

1.23 Catalyzed Vapor Phase Reaction

Table III-9 gives the data for all of the catalyzed vapor phase runs to generate H_2S. The catalyst used was an activated alumina, either MCB AX-610 or Spence 10A.

1.231 Experiments Without Water

Three runs were conducted without water, but feeding near-stoichiometric ratios of sulfur/methane, at 675°C and the rather low space velocity of 9.5 std. vol./vol./hr. They yielded up to 181 mole % H_2S, along with 74 mole % CS_2.

Because CS_2 was found to be unreactive as a reductant for SO_2 under power plant flue gas conditions, the remaining experiments on H_2S generation employed water as a co-reactant in order to suppress the formation of CS_2, and to increase the yield of H_2S.

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(2) Smith and Fisher, Ind. & Eng. Chem. Vol. 42, No. 4, p. 704, (1950).

1.232 Experiments With Water

In Runs G6 through G24 in Table III-9, mixtures of sulfur, methane and water were conducted over MCB AX-610 activated alumina catalyst at temperatures ranging from 588° to 715°C, and space velocities ranging from 16 to 450 std.vol./vol./hr. The feed ratios of sulfur to methane varied from 3.8 to 4.2 g-atom/g-mole; and water to methane, from 1.8 to 4.2 mole/mole.

Under these conditions the runs generally gave high yields of H_2S and CO_2, with minor amounts of COS, and little or no detectable CS_2. Higher temperatures and water/methane ratios above 3.5 tended to suppress both COS and CS_2 yields. At 715°C, space velocities as high as 450 std.vol/vol./hr. were still low enough to sustain methane conversions over 90%.

An optimum set of reaction conditions, i.e., 400 std.vol./vol./hr., 715°C, and H_2O/CH_4 ratio of 3.55 mole/mole, gave a 94% CH_4 conversion, a 371 mole % yield of H_2S (94.3% of theory), no detectable CS_2, and a 2 mole % yield of COS.

In Runs G25 and G26, Spence 10A activated alumina catalyst was used instead of MCB AX-610. The performances of the two catalysts were found to be comparable.

2. Experimental Methods

2.1 Apparatus

2.11 Reduction of Sulfur Dioxide

The bench scale reactor assemblies used for conducting the SO_2 reduction experiments are illustrated in Figures III-6 and 7.

In the earlier runs Assembly No. 1 was used. The reactor consisted of a one-inch stainless steel tube, containing the catalyst bed and an axial thermowell. The reactor was heated by means of tube furnace. Simulated flue gas plus hydrogen sulfide was fed by blending hydrogen sulfide, sulfur dioxide, air, and a bottled mixture containing carbon dioxide, nitrogen, oxygen, and sometimes sulfur dioxide. The H_2S and SO_2 rates were controlled by micrometer needle valves, and measured on capillary flowmeters. Flow rates of the other feed gases were controlled with needle valves and measured on rotameters. The gases were mixed in a feed manifold, which was heated just before entering the reactor. Steam was introduced by pumping water into the heated section of the feed manifold.

This equipment generally provided accurate control of feed rates, except for occasional fouling of the capillary flowmeters due to dirt or sulfur deposition by reaction of H_2S and SO_2.

To strip the catalyst, nitrogen or other stripping gases were passed over the heated catalyst bed, and the reactor effluent was chilled in an air-or water-cooled condenser to recover the sulfur.

The second sulfur dioxide reduction assembly, Figure III-7, was constructed to provide more flexibility in feed compositions and space velocities, more stable flow control, and to allow for visual observation of the catalyst during the run.

The reactor consisted of a 1-inch diameter x 30-inch long Vycor glass tube containing a ¼-inch axial thermowell. The flowrates of the individual feed components were controlled with constant-differential-type flow controllers, and measured on rotameters. Steam was introduced as in Assembly No. 1, by pumping water into the heated end of the feed manifold, or else by pumping water directly into the reactor head.

Nitrogen oxides were added by metering dilute NO_x-N_2 mixtures into the feed manifold. Hydrogen chloride, when added, was introduced by feeding a dilute hydrochloric acid solution instead of the water.

During the stripping cycles, sulfur was collected in one or more air-cooled condensers consisting of U-tubes 1 inch in diameter by 8 inch in length.

In the SO_2 reductions in which very accurate control of the H_2S/SO_2 feed ratio was required, the feed mixture was prepared by blending two pre-bottled gas mixtures. One bottled mixture contained H_2S and N_2; the other generally contained SO_2, CO_2, N_2, and O_2. The flowrate of each mixture was controlled using a constant-differential-type flow controller, and measured on a rotameter.

In operation, the flow rates of the individual feed components were allowed to stabilize, with the feed stream bypassing the reactor. The feed mixture was then switched into the reactor, and samples of feed and tail gas were periodically analyzed by gas chromatography.

At the end of the SO_2 reduction cycle, the reactor was heated and the sulfur stripped and recovered. Occasionally the reactor effluent was monitored by GC analysis during the stripping cycle.

2.12 Production of Hydrogen Sulfide

The bench scale assembly for hydrogen sulfide production is illustrated in Figure III-8.

Molten sulfur was pumped into the reactor with a B.I.F. Microfeeder plunger-type pump, which was maintained at 150°C by means of electrical heating tapes. Bottled methane was metered by measuring the pressure drop across a stainless steel capillary tube 5-foot long by 0.006 inch I.D. Water was fed using a syringe pump.

The reactor consisted of a 1-inch diameter stainless steel pipe jacketted by an electric furnace. The feed and exit lines were heated with electrical heating tapes. The exit line led to an air-cooled stainless steel condenser containing glass wool, followed by an ice-water cooled condenser, and finally a soap film meter for measuring the tail gas rate.

In operation, the tail gas was periodically sampled and analyzed by gas chromatography. Unconverted sulfur was recovered and weighed.

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING

Run No.	Original Run No.	Catalyst		Temperature, °C	Space Velocity(2) vol/vol/hr.	Nominal Feed Composition							
						mole %						ppm	
		History	Pretreatment(1)			H_2S	SO_2	N_2	H_2O	O_2	CO_2	NO_2	NO
		No Catalyst											
R1	2	--	--	250	~600	0.4	0.2	99.4	0	0	0	0	0
		Linde Molecular Sieve 3A, 10-16 mesh											
R2	106B	Fresh	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Linde Molecular Sieve 4A, 1/16" pellets											
R3	3	Fresh	none	250	3750	0.4	0.2	99.4	0	0	0	0	0
		Linde Molecular Sieve 4A, 10-20 mesh											
R4	94A	Fresh	none	110	2650	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Linde Molecular Sieve 5A, 10-20 mesh											
R5	105B	Fresh	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R6	109B	Fresh	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Norton Molecular Sieve Zeolon H, 4 x 8 mesh											
R7	72B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
		Davison Molecular Sieve REX, 4 x 8 mesh											
R8	78B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
		Davison Zeolitic Silica-Alumina XZ-25, 4 x 8 mesh											
R9	76B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
		Pittsburgh Activated Carbon Co. CAL Activated Carbon, 10-20 mesh											
R10	24	Fresh	none	200	11,560	0.4	0.2	75.4	6.0	3.8	14.2	0	0
R11	25-1	Run 24	none	180	11,560	0.4	0.2	75.4	6.0	3.8	14.2	0	0
R12	25-2	Run 25-1	none	140	11,560	0.4	0.2	75.4	6.0	3.8	14.2	0	0

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Run Time, min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	Initial or Average[3]
R1	250	1.78	30	0	in[4]
R2	140	1.98	6	4	av
R3	380	1.97	80	100	in
R4	260	1.83	24	53	av
R5	360	2.01	33	50	av
R6	120	2.20	51	94.6	av
R7	132	2	17	32	av
R8	171	-	13	57	av
R9	230	-	21	0	av
R10	120	2.01	83	-	in
R11	50	2.01	50	-	in
R12	60	2.01	26	-	in

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Original Run No.	Catalyst		Temperature, °C	Space Velocity$^{(2)}$ vol/vol/hr.	Nominal Feed Composition Mole %						ppm	
		History	Pre-treatment$^{(1)}$			H_2S	SO_2	N_2	H_2O	O_2	CO_2	NO_2	NO
Davison Silica Gel ID, 10 mesh													
R13	70B	Fresh	none	125	2960	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Davison Silica Gel RD, 3-8 mesh													
R14	71B	Fresh	none	125	2960	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R15	84B	Fresh	none	150	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R16	85B	Run 84B	none	100	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
PCR 150-5, 10% Fe_2O_3 on ID Silica Gel, 10 mesh													
R17	77B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
PCR 150-10, 10% TiO_2 on ID Silica Gel, 10 mesh													
R18	81B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
PCR 150-11, 10% Al_2O_3 on ID Silica Gel, 10 mesh													
R19	82B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
PCR 150-10-2, 10% ZrO_2 on ID Silica Gel, 10 mesh													
R20	83B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Engelhard Activated Bauxite, Porocel 10-20 mesh													
R21	26	Fresh	none	250	11,900	0.4	0.2	76.1	6.3	3.7	13.3	0	0
R22	27	Run 26	none	200	11,800	0.4	0.2	77.1	5.3	3.7	13.3	0	0
R23	28	Run 27	none	202	11,070	0.4	0.2	82.0	0	3.8	14.2	0	0
R24	29	Run 28	none	200	11,200	0.4	0.2	99.1	0	0	0	0	0
R25	31	Run 29	none	203	11,730	0.4	0.2	93.4	6.0	0	0	0	0
Engelhard Activated Bauxite, Porocel 6-10 mesh													
R26	79B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R27	80B	Run 79B	1	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Engelhard Activated Bauxite, Porocel LPD, 4-6 mesh													
R28	90B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R29	91B	Run 90B	2	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R30	92B	Fresh	none	150	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Englehard Activated Bauxite, Porocel 10-20 mesh													
R31	107B-1	Fresh	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R32	107B-2	Run 107B-1	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R33	108B	Fresh	none	110	3510	0.4	0.2	75.9	5.0	4.5	14.0	0	0

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Run Time, min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	Initial or Average(3)
R13	191	1.94	12	2	av
R14	231	3.15	36	13	av
R15	168	-	8	12	av
R16	310	-	5	50	av
R17	280	-	0.7	14	av
R18	183	-	3	5	av
R19	245	-	12	9	av
R20	216	-	0	17	av
R21	120	2.04	43	17	in
R22	125	2.10	16	7	in
R23	121	2.09	80	36	in
R24	121	4.04	49	96	in
R25	124	2.00	14	7	in
R25	230	-	91.9	100.	av
R27	280	-	49	71	av
R28	360	-	80	94.9	av
R29	138	-	44	50	av
R30	325	2.	40	48	av
R31	180	2.01	100.	100.	av
R32	180	2.00	72	67	av
R33	300	2.20	74	71	av

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Original Run No.	Catalyst		Temperature, °C	Space Velocity(2) vol/vol/hr.	Nominal Feed Composition							
		History	Pre-treatment(1)			Mole %						ppm	
						H_2S	SO_2	N_2	H_2O	O_2	CO_2	NO_2	NO
Davison Silica-Alumina 980, 4 x 8 mesh													
R34	75B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Matheson, Coleman and Bell Activated Alumina AX-610, 10-14 mesh													
R35	95B	Fresh	none	200	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R36	96B	Run 95B	none	225	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R37	97B	Run 96B	none	180	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R39	67	Fresh	none	125	3880	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R40	69	Run 67	3	125	3880	0.4	0.2	74.9	5.5	4.0	15.0	0	0
Alcoa Activated Alumina H-151, 1/8" spheres													
R41	68	Fresh	none	125	3770	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R42	70	Fresh	none	125	2380	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R43	71	Run 70	4	125	2380	0.4	0.2	74.9	5.5	4.0	15.0	0	0
Alcoa Activated Alumina F-1, 10-20 mesh													
R44	72	Fresh	none	125	2700	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R45	73	Run 72	5	125	2700	0.4	0.2	74.9	5.5	4.0	15.0	0	0
Alcoa Activated Alumina F-1, 6-10 mesh													
R46	93B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R47	94B	Run 93B	7	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Conoco High Area Alumina Catapal N-2, +10 mesh													
R48	74	Fresh	none	125	2740	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R49	75	Run 74	5	125	2740	0.4	0.2	74.9	5.5	4.0	15.0	0	0
Intsel Activated Alumina, Grade A, 3/16" spheres													
R50	86B	Fresh	none	125	3030	0.4	0.2	74.9	5.5	4.0	15.0	0	0
R51	87B	86B	6	125	3030	0.4	0.2	74.9	5.5	4.0	15.0	0	0
Davison High Area Alumina, SMR-7-2434, 4 x 8 mesh													
R52	88B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R53	89B	88B	6	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
Spence Activated Alumina Actal A, 10-20 mesh													
R54	41	Fresh	none	125	3910	0.4	0.2	76.7	5.5	3.7	13.6	0	0
R55	42	Run 41	8	125	2830	0.4	0.2	77.2	5.1	3.7	13.4	0	0
R56	43	Fresh	none	125	2875	0.4	0.2	76.6	5.0	3.5	14.3	0	0

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Run Time, min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	% Conversion Initial or Average(3)
R34	235	2.18	6	0.8	av
R35	360	-	48	38	av
R36	360	-	24	16	av
R37	360	-	5	21	av
R39	601	2.05	90	100.	av
R40	150	2.21	84	100.	av
R41	779	2.44	91.	95.5	av
R42	1104	2.22	94.	94.5	av
R43	446	1.88	92.	92.	av
R44	360	2.	>95	>95	av
R45	360	1.75	81	51	av
R46	360	2.	88	100.	av
R47	375	2.	57	89	av
R48	360	1.58	95	45	av
R49	360	1.93	86	56	av
R50	360	-	82	92.1	av
R51	224	-	58	79	av
R52	360	-	77	81	av
R53	255	-	17	66	av
R54	2145	1.95	98	97.4	in
R55	655	2.01	89	93.1	in
R56	1065	2.16	98.5	98.5	in

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Original Run No.	Catalyst History	Catalyst Pre-treatment(1)	Temperature, °C	Space Velocity(2) vol/vol/hr.	Nominal Feed Composition Mole % H_2S	SO_2	N_2	H_2O	O_2	CO_2	ppm NO_2	NO
		Linde Molecular Sieve 13X, 1/8" pellets											
R57	5	Fresh	none	252	3750	0.4	0.2	99.4	0	0	0	0	0
R58	6	Run 5	none	255	3750	0.4	0.2	99.4	0	0	0	0	0
R59	7	Run 6	none	253	3750	0.4	0.2	99.4	0	0	0	0	0
R60	8	Fresh	none	252	3750	0.4	0.2	99.4	0	0	0	0	0
R61	9	Run 8	none	247	3750	0.4	0.2	99.4	0	0	0	0	0
R62	10	Run 9	none	252	3750	0.4	0.2	99.4	0	0	0	0	0
R63	11	Run 10	none	255	3750	0.4	0.2	99.4	0	0	0	0	0
R64	12	Fresh	none	258	3750	0.4	0.2	99.4	0	0	0	0	0
R65	73B	Fresh	none	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
R66	74B	Run 73B	4	125	3030	0.4	0.2	75.9	5.0	4.5	14.0	0	0
		Linde Molecular Sieve 13X, 10-25 mesh											
R67	16	Fresh	none	246	7450	0.4	0.2	99.4	0	0	0	0	0
R68	17	Run 16	none	252	7450	0.4	0.2	99.4	0	0	0	0	0
R69	18	Run 17	none	258	7450	0.4	0.2	99.4	0	0	0	0	0
R70	19	Run 18	none	306	7450	0.4	0.2	99.4	0	0	0	0	0
R71	20	Run 19	none	412	7450	0.4	0.2	99.4	0	0	0	0	0
R72	21	Run 20	none	258	7850	0.4	0.2	75.4	6.0	3.8	14.2	0	0
R73	22	Run 21	none	250	7850	0.4	0.2	75.4	6.0	3.8	14.2	0	0
R74	23	Run 22	none	200	7850	0.4	0.2	75.4	6.0	3.8	14.2	0	0
		Linde Molecular Sieve 13X, 10-20 mesh											
R75	92A	Fresh	none	110	2620	0.4	0.2	75.9	5.0	4.5	14.0	50	450
R76	93A	Run 92A	9	110	2620	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Linde Molecular Sieve 13X, 25 mesh											
R77	13	Fresh	none	257	15,100	0.4	0.2	99.4	0	0	0	0	0
R78	14	Run 13	none	247	15,100	0.4	0.2	99.4	0	0	0	0	0
R79	15	Run 14	none	259	15,100	0.4	0.2	99.4	0	0	0	0	0

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Run Time, min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	Initial or Average(3)
R57	189	1.94	92.1	100.	in
R58	276	1.70	92.9	95.4	in
R59	206	1.82	75.2	79	in
R60	180	1.94	95.3	100.	in
R61	180	1.96	94.5	100.	in
R62	183	1.99	88.7	100.	in
R63	243	1.94	94.	100.	in
R64	150	2.00	51	59	in
R65	366	2.51	98.0	99.3	av
R66	365	2.27	60	77	av
R67	97	1.98	87	96	in
R68	120	1.94	90	100	in
R69	125	2.01	88	96	in
R70	121	1.96	86	97	in
R71	120	1.98	77	82	in
R72	66	2.01	19	35	in
R73	60	2.02	0	0	in
R74	120	2.02	0	0	in
R75	252	1.79	92.4	100.	av
R76	500	1.79	95.0	100.	av
R77	150	1.93	81	90	av
R78	151	1.94	79	91	av
R79	121	1.87	79	71	av

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

un o.	Original Run No.	Catalyst History	Catalyst Pre-treatment(1)	Temperature, °C	Space Velocity(2) vol/vol/hr.	Nominal Feed Composition, Mole % H_2S	SO_2	N_2	H_2O	O_2	CO_2	ppm NO_2	ppm NO
		Davison Molecular Sieve 542 (Type 13X), 4-8 mesh spheres											
80	110B	Fresh	none	110	2700	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Davison Molecular Sieve 542 (Type 13X), 6-8 mesh spheres											
81	111B	Fresh	none	110	2700	0.4	0.2	75.9	5.0	4.5	14.0	50	450
		Davison Molecular Sieve 542 (Type 13X), 10-20 mesh											
82	112B	Fresh	none	110	2700	0.4	0.2	75.9	5.0	4.5	14.0	50	450
83	113B	Run 112B	10	110	2700	0.4	0.2	75.9	5.0	4.5	14.0	50	450
84	114B	Run 113B	10	110	2700	0.4	0.2	75.9	5.0	4.5	14.0	50	450

TABLE III-1: REDUCTION OF SULFUR DIOXIDE AT POWER PLANT FLUE GAS CONCENTRATIONS: CATALYST SCREENING (Cont.)

Run No.	Run Time, min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion		
			H_2S	SO_2	Initial or Average(3)
R80	180	1.92	93.9	95.8	av
R81	360	1.92	93.0	94.3	av
R82	360	1.92	100.	100.	av
R83	360	2.00	100.	96.9	av
R84	360	1.95	100.	93.2	av

NOTES TO TABLE III-1

(1) Catalyst Pretreatment Code:

1: Stripped 5 hr @ 125-400°C in N_2
2: Stripped 5 hr @ 25-350°C in N_2
3: Stripped 4 hr @ 125-450°C in N_2
4: Stripped 7 hr @ 125-450°C in N_2
5: Stripped 6 hr @ 125-450°C in N_2
6: Stripped 6 hr @ 25-350°C in N_2
7: Stripped 3 hr @ 25-350°C in N_2
8: Stripped 12 hr @ 600°C in N_2
9: Stripped 2 hr @ 500°C in N_2; then hydrated 1 hr @ 110° in 5% H_2O, 95% N_2
10: Stripped 2-3 hr @ 500°C in 1% H_2S, 99% N_2

(2) Space Velocity = vol. of feed at 25°C, 1 at./bulk vol. of catalyst bed/hr.

(3) Average conversion measured during first 360 min. of run, or entire run, whichever is less.

(4) Small amount of sulfur visibly formed in this run.

TABLE III-2: CATALYST SCREENING RESULTS, LOW TEMPERATURE SO_2 REDUCTION

Feed Composition: 0.4% H_2S, 0.2% SO_2, 5-6% H_2O, 4-5% O_2, 13-15% CO_2, balance N_2

Temperatures: within the range 110°-135°C.

Good or Excellent:

- Molecular Sieves Type 13X
  - Linde 13X
  - Davison 542
- Activated Aluminas
  - Spence Actal A
  - Matheson, Coleman and Bell AX-610
  - Alcoa H-151
  - Alcoa F-1
  - Conoco Catapal N-2
  - Intsel Grade A
- Activated Bauxites
  - Engelhard Porocel Sulfur Recovery Catalyst
  - Engelhard Porocel LPD

Poor, but Showed Some Activity:

- Molecular Sieve 4A (Linde)
- Molecular Sieve 5A (Linde)
- Molecular Sieve Zeolon H (Norton H-exchanged Zeolite)
- Molecular Sieve REX (Davison rare-earth exchanged Zeolite)
- Silica Gel RD (Davison)
- High Area Alumina (Davison SMR-7-2434)
- Silica-Alumina (Davison 980)

Poor, Showed Low or Negligible Activity

- Silica Gel ID (Davison)
- 10% Fe_2O_3 on Silica Gel
- 10% TiO_2 on Silica Gel
- 10% Al_2O_3 on Silica Gel
- 10% ZrO_2 on Silica Gel
- Zeolitic Silica-Alumina (Davison XZ-25)
- Molecular Sieve 3A (Linde)

TABLE III-3: CATALYST REACTIVATION STUDIES

Catalyst: Spence Activated Alumina Actal A, 10-20 mesh.

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75-79% N_2, 3.3 to 5.7% H_2O, 3.5 to 4.5% O_2, 13.2 to 14.3% CO_2

Run No.	Original Run No.	Catalyst History	Catalyst Pretreatment Time, hr.	 Temperature, °C	 Atmosphere	 Additional Pretreatment[1]
R85	35	Fresh	(none)			
R86	36	Run 35	Several	600	N_2	-
R87	37	Run 36	Several	600	N_2	-
R88	38	Run 37	Several	600	N_2	-
R89	40	Run 39	Several	600	N_2	-
R54	41	Fresh	(none)			
R55	42	Run 41	12	600	N_2	-
R56	43	Fresh	(none)			
R90	44	Run 43	4	500	N_2	-
R91	45	Run 44	4	460	N_2	1
R92	46	Run 45	3	460	N_2	2
R93	47	Fresh	(none)			
R94	48	Run 47	3 to 6	275	N_2	-
R95	49	Run 48	3 to 6	275	N_2	-
R96	50	Run 49	3 to 6	275	N_2	-
R97	51	Run 50	3 to 6	275	N_2	-
R98	58	Fresh	(none)			
R99	59	Run 58	6	275	25% H_2O, 75% N_2	-
R100	60	Run 59	6	275	25% H_2O, 75% N_2	-
R101	61	Run 60	3.5	275	25% H_2O, 75% N_2	-
R102	62	Run 61	18	275	N_2	3
R103	63	Run 62	1	525	N_2	4
R104	64-1	Fresh	1.5	525	N_2	-
R105	64-2	Run 64-1	1.5	125 to 525	N_2	4
R106	65	Fresh	(none)			
R107	66	Fresh	(none)			

TABLE III-3: CATALYST REACTIVATION STUDIES (Cont.)

Catalyst: Spence Activated Alumina Actal A, 10-20 mesh.

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75-79% N_2, 3.3 to 5.7% H_2O, 3.5 to 4.5% O_2, 13.2 to 14.3% CO_2

SO_2 Reduction Cycle

Run No.	Temperature, °C	Space[(2)] Velocity, Vol./Vol./hr.	Run Time min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	Initial or Average[(3)]
R85	150	8880	145	2.07	85	87.5	in
R86	200	8860	127	1.95	70	61	in
R87	110-130	9330	120	1.97	65	68	in
R88	125	9330	410	1.71	61	81	in
R89	120-125	8560	430	1.82	53	42	in
R54	125	2910	2145	1.95	98	97	in
R55	125	2830	655	2.01	89.5	93	in
R56	125	2870	1065	2.16	98.5	98.5	in
R90	125	2860	1075	2.04	97	98	in
R91	125	2850	550	2.23	92.2	91.4	in
R92	125	2930	437	2.26	82	85	in
R93	125	2920	485	1.98	98.5	99	in
R94	125	2920	570	2.21	94	97	in
R95	125	2920	485	2.01	84	87	in
R96	135	2920	265	2.11	79	65	in
R97	125	2920	370	1.83	86	98	in
R98	125	2930	405	1.85	100	100	in
R99	125	2930	480	1.87	91	86	in
R100	125	2930	460	1.72	58	50	in
R101	125	2900	130	1.72	73	43	in
R102	125	2900	132	1.65	56	0	in
R103	125	2900	170	1.74	54	22	in
R104	125	2900	486	1.87	95.5	98	av
R105	125	2900	90	1.78	88	87.5	av
R106	125	2900	874	1.78	97.5	90	av
R107	125	2900	745	1.78	99.5	93	av

TABLE III-3: CATALYST REACTIVATION STUDIES (Cont.)

Catalyst: Matheson, Coleman & Bell Activated Alumina AX-610, 10-14 mesh

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

			Catalyst Pretreatment			
Run No.	Original Run No.	Catalyst History	Time, hr.	Temperature, °C	Atmosphere	Additional Pretreatment(1)
R108	8A	Fresh	(none)			
R109	9A	Run 8A	5	125-300	N_2	-
R110	10A	Run 9A	5	125-300	N_2	-
R111	16A	Run 10A	7.5	25-400	N_2	5
R112	11A	Fresh	(none)			
R113	12A	Run 11A	7.5	125-450	N_2	-
R114	13A	Run 12A	7	125-500	N_2	-
R115	15A	Run 13A	6	25-550	N_2	6
R116	14A	Fresh	(none)			
R117	17A	Run 14A	7.5	25-400	N_2	-
R118	18A	Run 17A	4	25-400	N_2	7
R119	19A	Run 18A	4	25-400	N_2	7
R120	20A	Fresh	(none)			
R121	21A	Run 20A	6	25-400	N_2	8
R122	22A	Run 21A	5	125-400	N_2	9
R123	23A	Run 22A	2	125-320	N_2	-
R124	24A	Fresh	(none)			
R125	25A	Run 24A	7-8	100-400	N_2	-
R126	26A	Run 25A	7-8	100-400	N_2	-
R127	27A	Fresh	(none)			
R128	28A	Run 27A	2.5-6	25-350	N_2	10
R129	29A	Run 28A	2.5-6	25-350	N_2	10
R130	30A	Run 29A	2.5-6	25-350	N_2	10
R131	31A	Run 30A	2.5-6	25-350	N_2	10
R132	32A	Run 31A	2.5-6	25-350	N_2	10

TABLE III-3: CATALYST REACTIVATION STUDIES (Cont.)

Catalyst: Matheson, Coleman & Bell Activated Alumina AX-610, 10-14 mesh

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

SO_2 Reduction Cycle

Run No.	Temperature, °C	Space Velocity,[2] Vol./Vol./hr.	Run Time min.	Measured Feed Ratio, Molar H_2S/SO_2	% Conversion H_2S	% Conversion SO_2	Initial or Average[3]
R108	125	2620	365	1.73	99.6	89.5	av
R109	125	2620	725	2.02	55.1	56.8	av
R110	125	2620	150	2.02	<50	<50	av
R111	125	2620	360	1.82	93.9	82.6	av
R112	125	2620	372	2.08	99.7	98.9	av
R113	125	2620	200	1.70	56.5	69.4	av
R114	125	2620	300	1.73	24.6	61.8	av
R115	125	2620	150	1.66	20.8	41.4	av
R116	125	2620	360	1.71	94.5	100	av
R117	125	2620	368	2.11	95.4	87.6	av
R118	125	2620	376	2.64	76.2	83.0	av
R119	125	2620	122	2.11	80.2	69.7	av
R120	125	2620	406	-	91.7	100	av
R121	125	2620	376	-	90.6	89.9	av
R122	125	2620	283	-	79.2	54.7	av
R123	125	2620	280	-	73.9	83.7	av
R124	125	2620	375	-	99.4	99.6	av
R125	125	2620	363	-	67.9	80.6	av
R126	125	2620	254	-	<50	<50	av
R127	125	2620	360	-	100	100	av
R128	125	2620	360	-	100	92.7	av
R129	125	2620	362	-	95.6	84.3	av
R130	125	2620	370	-	87.7	79.7	av
R131	125	2620	360	-	86.0	79.0	av
R132	125	2620	320	-	62.0	46.6	av

TABLE III-3: CATALYST REACTIVATION STUDIES (Cont.)

Catalyst: Matheson, Coleman & Bell Activated Alumina AX-610, 10-14 mesh

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

			Catalyst Pretreatment			
Run No.	Original Run No.	Catalyst History	Time, hr.	Temperature, °C	Atmosphere	Additional Pretreatment(1)
R133	33A	Fresh	(none)			
R134	34A	Run 33A	3	110-350	N_2	-
R135	35A	Run 34A	3	110-350	N_2	-
R136	36A	Run 35A	3	110-350	N_2	-
R137	37A	Run 36A	0.6	350	N_2	-
R138	38A	Run 37A	0.6	350	N_2	-
R139	39A	Run 38A	2	500	H_2S	11
R140	40A	Run 39A	2	500	H_2S	11
R141	41A	Run 40A	2	500	H_2S	11
R142	42A	Run 41A	2	500	H_2S	11
R143	43A	Run 42A	2	500	H_2S	11
R144	44A	Run 43A	2	500	H_2S	11
R145	45A	Run 44A	2-2.5	500	0.5% H_2S+99.5% N_2	12
R146	46A	Run 45A	2-2.5	500	10% H_2S+90% N_2	12
R147	47A	Run 46A	2-2.5	500	2% H_2S+98% N_2	12
R148	48A	Run 47A	3	110-500	5% H_2S+95% N_2	-
R149	49A	Run 48A	3	110-500	5% H_2S+95% N_2	-
R150	50A	Fresh	(none)			
R151	51A	Run 50A	1	500	N_2	-
R152	52A	Run 51A	1	500	N_2	-
R153	53A	Run 52A	1-6	500	15% H_2S+85% N_2	13
R154	54A	Run 53A	1	500	N_2	-
R155	55A	Run 54A	1.5-3.5	500	10% H_2S+90% N_2	-
R156	56A	Run 55A	1.5-3.5	500	10% H_2S+90%N_2	-

TABLE III-3: CATALYST REACTIVATION STUDIES (Cont.)

Catalyst: Matheson, Coleman & Bell Activated Alumina AX-160, 10-14 mesh

Nominal Feed Composition, mole %: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

			SO_2 Reduction Cycle				
					% Conversion		
Run No.	Temperature, °C	Space$^{(2)}$ Velocity, Vol./Vol./hr.	Run Time min.	Measured Feed Ratio, Molar H_2S/SO_2	H_2S	SO_2	Initial or Average$^{(3)}$
R133	110	2620	360	-	98.0	100.0	av
R134	110	2620	361	-	91.4	96.6	av
R135	110	2620	430	-	80.5	86.7	av
R136	110	2620	361	-	64.1	61.7	av
R137	110	2620	360	-	67.5	62.7	av
R138	110	2620	346	-	60.0	60.0	av
R139	110	2620	375	-	100.0	100.0	av
R140	110	2620	415	-	99.5	100.0	av
R141	110	2620	360	-	81.2	93.1	av
R142	110	2620	302	-	71.2	73.3	av
R143	110	2620	355	-	100.0	100.0	av
R144	110	2620	215	-	84.0	86.0	av
R145	110	2620	410	-	95.2	98.5	av
R146	110	2620	315	-	97.9	96.4	av
R147	110	2620	270	-	93.1	74.8	av
R148	110	2620	235	-	98.2	100.0	av
R149	110	2620	365	1.60	94.7	93.6	av
R150	110	2620	370	1.27	99.6	91.8	av
R151	110	2620	371	1.31	99.7	94.6	av
R152	110	2620	284	1.10	97.7	93.4	av
R153	110	2620	412	0.61	100.0	65.1	av
R154	110	2620	350	1.70	98.7	99.1	av
R155	110	2620	386	1.99	99.2	100.0	av
R156	110	2620	322	1.37	94.3	94.4	av

NOTES TO TABLE III-3

(1) Additional Pretreatment Code

1: followed by 12 hrs. @ 600°C in N_2
2: followed by 2 hrs. @ 600°C in N_2
3: followed by 2 hrs. @ 125°C in 95% N_2 + 5% H_2O
4: followed by 3 hrs. @ 525°C in air
5: followed by washing with water and then drying at 125°C
6: followed by 18 hrs. @ 650°C in air
7: preceded by 18 hrs. @ 25°C in air
8: preceded by 18 hrs. @ 25°C in 95% N_2 + 5% H_2O
9: preceded by 18 hrs. @ 125°C in N_2
10: preceded by 18 hrs. @ 25°C in N_2
11: preceded by 0.6-2 hrs. @ 350°C in N_2
12: preceded by 2.5 hrs. @ 110-350°C in N_2
13: preceded by 0.8 hrs. @ 500°C in N_2

(2) Space velocity = vol. of feed at 25°C, 1 at./bulk vol. of catalyst bed/hr.

(3) Average conversion measured for first 360 min. of run, or entire run, whichever is less.

TABLE III-4: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, ACTIVATED ALUMINA CATALYST

Catalyst: Matheson, Coleman and Bell Activated Alumina AX-610, 10-20 mesh

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

Space Velocity: 2620 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

		Catalyst					Conversion, %		
Run No.	Original Run No.	History	Pre-treatment(1)	Addition to Feed	Run Time, min.	Average Measured Molar Feed Ratio, H_2S/SO_2	Time, min.	H_2S	SO_2
R157	78A	Fresh	none	500 ppm HNO_3	575	1.48	(average)(2)	96.8	92.7
R158	79A	Run 78A	1	500 ppm HNO_3	320	1.36	(average)(2)	87.8	68.8
R159	80A	Run 79A	2	500 ppm HNO_3	709	1.53	(average)(2)	98.8	84.4
R160	81A-1	Run 80A	2	none	120	1.48	(average)(2)	100.0	100.0
R161	81A-2	Run 81A-1	none	225 ppm HCl	425	1.48	(average)(2)	100.0	96.5
R162	82A	Run 81A-2	2	225 ppm HCl	263	1.53	(average)(2)	90.8	98.1
R163	83A	Fresh	none	50 ppm NO_2+ 450 ppm NO	290	1.82	14	100.	100.
							72	100.	100.
							159	71.3	60.8
							244	83.5	65.9
							274	83.2	69.2
							Avg.	87.6	79.2
R164	84A-1	Run 83A	2	none	120	2.06	3	100.	100.
							36	100.	100.
							100	100.	
							Avg.	100.	100.
R165	84A-2	Run 84A-1	none	500 ppm NO	280	2.06	4	100.	100.
							80	87.5	76.6
							143	68.9	76.6
							230	65.5	56.6
							Avg.	80.5	77.4

TABLE III-4: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, ACTIVATED ALUMINA CATALYST (Cont.)

Catalyst: Matheson, Coleman and Bell Activated Alumina AX-610, 10-20 mesh

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 5.0% H_2O, 4.5% O_2, 14.0% CO_2

Space Velocity: 2620 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

Run No.	Original Run No.	Catalyst History	Catalyst Pre-treatment(1)	Addition to Feed	Run Time, min.	Average Measured Molar Feed Ratio H_2S/SO_2	Conversion, % Time, min.	Conversion, % H_2S	Conversion, % SO_2
R166	85A-1	Run 84A-2	2	500 ppm NO	160	1.93	10	100.	100.
							112	79.4	81.2
							160	67.7	74.9
							Avg.	82.4	85.4
R167	85A-2	Run 85A-1	none	none	390	1.93	51	49.9	78.9
							81	54.7	69.9
							143	60.2	75.3
							169	78.4	100.
							240	78.4	93.1
							345	62.7	58.9
							390	47.9	58.8
							Avg.	61.7	76.4
R168	86A	Run 85A-2	2	50 ppm NO_2	215	1.92	25	83.3	100.
							122	100.	100.
							155	100.	100.
							215	98.4	100.
							Avg.	95.4	100.
R169	87A	Run 86A	2	500 ppm NO_2	403	2.06	66	88.5	82.1
							154	95.3	98.0
							271	71.5	39.7
							403	66.0	6.0
							Avg.	80.3	56.4
R170	88A	Run 87A	2	50 ppm NO_2 + 500 ppm NO	253	2.16	16	91.3	100.
							132		83.8
							253	49.4	39.8

TABLE III-4: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, ACTIVATED ALUMINA CATALYST (Cont.)

NOTES TO TABLE III-4

(1) Catalyst Pretreatment Code

1: Stripped 4 hr @ 110-380°C in 10% H_2S + 90% N_2

2: Stripped 1.2 to 3.5 hr @ 110-500°C in 10% H_2S + 90% N_2

(2) Averaged during entire period of run.

TABLE III-5: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, MOLECULAR SIEVE 13X - TYPE CATALYST

Catalyst: Linde Molecular Sieve 13X

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14% CO_2, 5.0% H_2O

Space Velocity: 2620 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

Run No.	Original Run No.	Catalyst			Addition to Feed	Run Time Min.	Measured Molar Feed Ratio, H_2S/SO_2		Conversion, %		
		Pellet Size	History	Pre-treatment (1)			Time, min.	Ratio	Time, Min.	H_2S	SO_2
R171	89A	4x8 mesh	Fresh	none	50 ppm NO_2+ 450 ppm NO	343	43	2.34	8	80.6	100.
							178	2.14	134	87.0	100.
							310	2.19	276	78.5	98.9
									343	90.3	97.8
R172	90A	4x8 mesh	Fresh	none	50 ppm NO_2+ 450 ppm NO	501	97	1.68	49	91.5	100.
							198	2.16	130	90.2	100.
							339	2.17	164	83.8	100.
									259	93.5	91.3
									377	82.6	92.4
									430	80.1	90.7
									501	84.5	85.7
R173	91A	4x8 mesh	Run 90A	1	50 ppm NO_2+ 450 ppm NO	465	100	1.94	16	83.8	100.
							141	1.98	66	86.3	100.
							255	2.05	214	92.4	96.9
							275	1.94	348	82.7	88.5
									432	-	81.3
									465	71.6	81.7
R75	92A	10-20 mesh	Fresh	none	50 ppm NO_2+ 450 ppm NO	252	100	1.94	34	86.6	100.
							224	2.02	69	95.9	100.
							291	2.21	192	94.6	100.
							332	2.11	252	92.6	100.

TABLE III- 5: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, MOLECULAR SIEVE 13X - TYPE CATALYST (Cont.)

Catalyst: Linde Molecular Sieve 13X

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14% CO_2, 5.0% H_2O

Space Velocity: 2620 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

Run No.	Original Run No.	Catalyst Pellet Size	Catalyst History	Catalyst Pre-treatment[(1)]	Addition to Feed	Run Time Min.	Measured Molar Feed Ratio, H_2S/SO_2 Time, min.	Measured Molar Feed Ratio, H_2S/SO_2 Ratio	Conversion, % Time, Min.	Conversion, % H_2S	Conversion, % SO_2
R76	93A	10-20 mesh	Run 92A	1	50 ppm NO_2+	500	14	1.43	45	100.	100.
					450 ppm NO		78	1.44	108	100.	100.
							135	1.71	177	84.0	100.
							151	2.34	241	91.0	100.
							211	1.84	340	100.	100.
							269	2.00	418	94.4	100.
							375	1.64	500	88.8	100.
							451	2.19			
R174	95A	10-20 mesh	Run 93A	1	50 ppm NO_2+	343	0	1.99	16	100.	100.
					450 ppm NO		46	1.73	81	95.3	100.
							440	2.70	162	100.	100.
									197	97.1	100.
									343	95.7	100.
R175	96A	10-20 mesh	Run 95A	1	50 ppm NO_2+	391	122	2.15	53	87.6	100.
					450 ppm NO		170	1.98	87	91.4	100.
							245	1.84	209	84.1	100.
									312	86.7	100.
									391	85.6	100.
R176	97A	10-20 mesh	Run 96A	2	50 ppm NO_2+	425	11	2.27	45	82.6	100.
					450 ppm NO		76	1.65	127	-	100.
							141	1.45	202	91.4	100.
							154	2.46	277	-	100.
							326	1.76	360	85.7	100.
									425	-	100.

TABLE III-5: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2, MOLECULAR SIEVE 13X - TYPE CATALYST (Cont.)

Catalyst: Linde Molecular Sieve 13X

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14% CO_2, 5.0% H_2O

Space Velocity: 2620 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

Run No.	Original Run No.	Catalyst Pellet Size	Catalyst History	Catalyst Pre-treatment(1)	Addition to Feed	Run Time, Min.	Measured Molar Feed Ratio, H_2S/SO_2 Time, min.	Measured Molar Feed Ratio, H_2S/SO_2 Ratio	Conversion, % Time, Min.	Conversion, % H_2S	Conversion, % SO_2
R177	98A	10-20 mesh	Run 97A	2	50 ppm NO_2+	392	34	2.37	119	91.3	100.
					450 ppm NO		79	1.55	194	93.4	100.
							163	1.63	250	86.6	100.
							200	1.85	392	94.6	99.6
							225	1.80			
							283	2.07			
R178	99A	10-20 mesh	Run 98A	2	50 ppm NO_2,	325	14	1.76	127	90.4	100.
					450 ppm NO,		45	2.12	160	90.4	100.
					100 ppm HCl		133	2.10	191	92.6	100.
							295	2.04	265	92.8	100.
									325	97.6	100.
R179	100A	10-20 mesh	Run 99A	2	50 ppm NO_2,	373	12	1.81	160	100.	100.
					450 ppm NO,		53	1.45	231	100.	100.
					100 ppm HCl		190	1.50	305	93.7	91.2
							265	1.94	373	94.1	87.2

TABLE III-5: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2 MOLECULAR SIEVE 13X - TYPE CATALYST (Cont.)

Catalyst: Davison 542

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14.0% CO_2, 5.0% H_2O

Space Velocity: 2700 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

Run No.	Original Run No.	Catalyst Pellet Size	Catalyst History	Catalyst Pre-treatment(1)	Addition to Feed	Run Time, Min.	Measured Average Feed Ratio, H_2S/SO_2	Time, Min.	Conversion, % H_2S	Conversion, % SO_2
R80	110B	4-8 mesh spheres	Fresh	none	50 ppm NO_2 + 500 ppm NO	180	1.92	60	100.	100.
								120	91.4	95.7
								180	90.2	91.7
								Avg.	93.9	95.8
R81	111B	6-8 mesh spheres	Fresh	none	50 ppm NO_2 + 500 ppm NO	360	1.92	60	100.	100.
								120	94.8	100.
								180	91.5	97.9
								240	92.3	93.6
								300	91.2	89.1
								360	88.3	85.1
								Avg.	93.0	94.3

TABLE III-5: EFFECTS OF NO_x AND HCl ON THE CATALYTIC REDUCTION OF SO_2
MOLECULAR SIEVE 13X - TYPE CATALYST (Cont.)

Catalyst: Davison 542

SO_2 Reduction Conditions:

Temperature: 110°C

Nominal Feed Composition: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2, 14.0% CO_2, 5.0% H_2O

Space Velocity: 2700 vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr.

		Catalyst						Conversion, %		
Run No.	Original Run No.	Pellet Size	History	Pre-treatment(1)	Addition to Feed	Run Time, Min.	Measured Average Feed Ratio, H_2S/SO_2	Time, Min.	H_2S	SO_2
R82	112B	10-20 mesh	Fresh	none	50 ppm NO_2 + 500 ppm NO	360	1.92	60	100.	100.
								120	100.	100.
								180	100.	100.
								240	100.	100.
								300	100.	100.
								360	100.	100.
								Avg.	100.	100.
R83	113B	10-20 mesh	Run 112B	3	50 ppm NO_2 + 500 ppm NO	360	2.00	60	100.	100.
								120	100.	100.
								180	100.	100.
								240	100.	100.
								300	100.	93.2
								360	100.	88.2
								Avg.	100.	96.9
R84	114B	10-20 mesh	Run 113B	4	50 ppm NO_2 + 500 ppm NO	360	1.95	60	100.	100.
								120	100.	100.
								180	100.	100.
								240	100.	89.4
								300	100.	87.6
								360	100.	82.4
								Avg.	100.	93.2

NOTE TO TABLE III-5

(1) **Catalyst Pretreatment Code:**

1: Stripped 2 hr. @ 500°C in 10% H_2S + 90% N_2; then hydrated 1 hr. @ 110° in 5% H_2S + 95% N_2

2: Same as 1, but hydration step omitted.

3: Stripped 2 hr. @ 500°C in 1% H_2S + 99% N_2.

4: Stripped 3 hr. @ 500°C in 1% H_2S + 99% N_2.

TABLE III - 6

H_2S EMISSION CONTROL: EFFECTS OF H_2S/SO_2 RATIO ON H_2S EXIT CONCENTRATION FROM AN SO_2 REDUCTION REACTOR

Catalyst: MCB's AX-610 Activated Alumina
Temperature: 110°C
Space Velocity: ~3000 std. vol/vol/hr.
Simulated flue gas composition, containing ~0.2% SO_2, 14% CO_2, 4.5% O_2, ~76% N_2, and 5% H_2O.

Run No.	Orig. Run No.	Time of Run, min.	Measured Feed Ratio H_2S/SO_2 (molar)	Time of Run, min.	H_2S Exit Concentration, ppm
R180	101B	115	2.05	120	64
		180	1.72	180	50
		300	1.78	240	39
		330	1.79	300	35
		360	1.74	360	38
		Avg.	1.82	Avg.	45
R181	99B	40	1.84	60	76
		72	1.76	120	47
		110	1.88	180	50
		140	1.89	Avg.	58
		180	1.85		
		Avg.	1.84		
R182	104B	60	2.10	120	59
		100	1.86	180	61
		120	1.97	240	60
		180	2.03	300	47
		240	1.97	Avg.	57
		260	1.84		
		300	1.83		
		Avg.	1.94		
R183	100B	45	2.10	60	82
		90	2.04	90	80
		120	2.06	120	69
		135	2.09	180	68
		240	2.04	240	55
		Avg.	2.06	Avg.	71
R184	98B	35	2.14	211	92
		95	2.05	302	56
		130	2.14	361	135
		180	2.09	Avg.	95
		220	2.10		
		330	2.20		
		Avg.	2.12		
R185	102B	60	2.48	120	142
		125	2.30	180	127
		180	2.25	240	124
		240	2.28	300	122
		300	2.28	Avg.	128
		Avg.	2.32		

TABLE III - 6 (Cont.)

H_2S EMISSION CONTROL: EFFECTS OF H_2S/SO_2 RATIO ON H_2S EXIT CONCENTRATION FROM AN SO_2 REDUCTION REACTOR

Catalyst: MCB's AX-610 Activated Alumina
Temperature: 110°C
Space Velocity: ~3000 std. vol/vol/hr.
Simulated flue gas composition, containing ~0.2% SO_2, 14% CO_2, 4.5% O_2, ~76% N_2, and 5% H_2O.

Run No.	Orig. Run No.	Time of Run, min.	Measured Feed Ratio H_2S/SO_2 (molar)	Time of Run, min.	H_2S Exit Concentration, ppm
R186	103B	60	2.84	120	259
		120	2.86	180	225
		180	2.84	240	237
		240	2.84	300	177
		300	2.93	360	237
		360	2.92		
		Avg.	2.87	Avg.	227

TABLE III-7:

REDUCTION OF SULFUR DIOXIDE BY HYDROGEN SULFIDE IN A SIMULATED SMELTER GAS COMPOSITION

Catalyst: MCB's AX-610 Activated Alumina, 10-14 mesh

Feed Composition (Nominal): 11.3% SO_2, 22.6% H_2S, 5.7% CO_2, 0.88% O_2, 59.5% N_2

Run No.	Original Run No.	Temperature, °C	Space Velocity, Vol./Vol./Hr.	Run Time, min.	H_2S/SO_2 Avg. Measured Feed Ratio	Catalyst History	Average % Conversion H_2S	Average % Conversion SO_2
R187	66A	250	4100	140	2.06	Run 64A	96.8	89.5
R188	67A	250	4100	290	1.84	Run 66A	90.7	84.0
R189	68A	270	4100	420	2.06	Run 67A	87.9	92.0
R190	69A	275	4100	375	1.89	Run 68A	88.0	90.2
R191	70A	275	4100	200	1.72	Run 69A	87.7	95.5
R192	57A	300	4100	195	1.22	Fresh	100.0	67.4
R193	58A	300	4100	120	1.80	Run 57A	98.8	93.4
R194	59A	300	4100	270	1.67	Run 58A	100.	-
R195	60A	300	4100	97	1.42	Run 59A	97.0	97.9
R196	61A	300	4100	240	2.16	Run 60A	95.0	92.3
R197	62A	350	4100	260	2.07	Run 61A	95.8	88.3
R198	63A	350	4100	160	1.94	Run 62A	92.4	84.4
R199	64A	350	4100	250	1.98	Run 63A	93.1	84.5
R200	71A	300	1400	360	2.23	Fresh	95.9	98.2
R201	72A	300	1400	325	2.13	Run 71A	95.0	95.7
R202	73A	350	1400	360	1.95	Run 72A	98.5	91.0
R203	74A	350	1400	340	1.84	Run 73A	98.0	87.5
R204	75A	350	1400	365	2.25	Run 74A	93.9	96.6
R205	76A	400	1400	360	2.70	Run 75A	91.1	97.4

TABLE III-8: GENERATION OF HYDROGEN SULFIDE: UNCATALYZED VAPOR PHASE REACTION OF METHANE AND SULFUR

Space velocity: 13.6 vol. of feed @ 25°C, 1 at./vol. of reactor/hr. (based on sulfur as S_2)

Run No.	Original Run No.	Temperature, °C	Feed Rates S g.atom/hr.	 CH_4 g.mole/hr.	Feed Ratio S/CH_4 g. atom/mole	% Conversion CH_4	Yield mole/mole of CH_4 Fed H_2S	 CS_2	Material Balances, % Product/Feed C	 H
31	8	596	0.167	0.043	3.88	16	0.32	-	88	-
32	9	607	0.167	0.044	3.80	36	0.66	0.29	93	97

TABLE III-9: GENERATION OF HYDROGEN SULFIDE: CATALYZED VAPOR PHASE REACTION OF METHANE AND SULFUR

	Original Run No.	Temperature, °C	Space Velocity Vol./Vol./hr.(1)	Catalyst Bed wt. g	Feed Ratios S/CH_4 g-atom/mole	Feed Ratios H_2O/CH_4 mole/mole
		Catalyst: Matheson, Coleman & Bell Activated Alumina AX-610, 8-9 mesh				
G3	10	675	9.50	160*	3.92	0
G4	11	665	9.55	160	3.75	0
G5	13	622	9.45	218*	4.17	0
G6	16	604	16.2	218	4.14	1.82
G7	17	610	16.6	218	4.04	1.96
G8	18	696	17.5	209*	3.65	≫2
G9	19	696	17.5	209	3.65	≫2
G10	20	696	20.2	209	3.87	2.06
G11	21	671	22.2	178*	3.87	2.06
G12	22	671	34.0	178	3.84	2.01
G13	23	681	68	100*	3.84	2.01
G14	24	681	68	100	3.84	2.01
G15	25	588	68	100	3.75	1.94
G16	26	672	330	20*	3.84	2.06
G17	27	715	330	20	3.96	2.14
G18	28	690	330	20	3.83	2.06
G19	29	691	450	20	3.83	3.95
G20	30	715	450	20	4.08	4.18
G21	31	715	450	20	4.13	4.33
G22	32	715	400	20	4.16	3.55
G23	33	715	360	20	4.14	2.13
G24	34	715	330	20	4.14	2.14
		Catalyst: Spence Activated Alumina 10A, 8-9 mesh				
G25	36	715	330	20*	4.16	2.16
G26	37	715	400	20	4.70	3.68

* Fresh catalyst charge

Note: (1) Vol. of feed @ 25°C, 1 at./bulk vol. of catalyst bed/hr., based on sulfur as S_6.

TABLE III-9: GENERATION OF HYDROGEN SULFIDE: CATALYZED VAPOR PHASE REACTION OF METHANE AND SULFUR (Cont.)

	Original Run No.	% Conversion		Yield(2), mole % Based on Mole CH_4 Fed				Material Balances % Product/Feed			
		CH_4	S	H_2S	CO_2	COS	CS_2	C	H	S	O
	Catalyst: Matheson, Coleman & Bell Activated Alumina AX-610, 8-9 mesh										
G3	10	90		181			74				
G4	11	75		157			68				
G5	13	95		174			78				
G6	16	91.2									
G7	17	78		310	73			95	89	85	79
G8	18	99.5		278	74			77		77	
G9	19	99.4	100.								
G10	20	100.									
G11	21	99.5									
G12	22	99									
G13	23	98	97								
G14	24	99	97.5								
G15	25	54.5	42.5	148	40	1	0	86.2	75	97	70
G16	26	83.2	80	318	64	9	1	91	99	106	90
G17	27	97.5	94	326	29	43	7	81	81	103	48
G18	28	92.8	90.4	351	49	18	1	75.4	96.7	106	70.1
G19	29	82.7	73.9	300	70	2	0	87.3	87.8	102	82.9
G20	30	90.7		343	76	1	0	87.3	-	-	-
G21	31	92.6	89.6	361	82	3	0	85.3	97.0	98.5	90.6
G22	32	94	85.2	371	82	2	0	88.5	102.	104	96.5
G23	33	97.4	90.2	368	76	5	0	83.6	93.6	99.8	83.0
G24	34	98.3	83.5	353	70	8	0	97.9	86.9	100.8	85.4
	Catalyst: Spence Activated Alumina 10A, 8-9 mesh										
G25	36	98.4	92.4	376	71	14	0	86.5	95.7	103	81.2
G26	37	94.6	91.0	377	77	4	0	86.0	106	90.0	100.

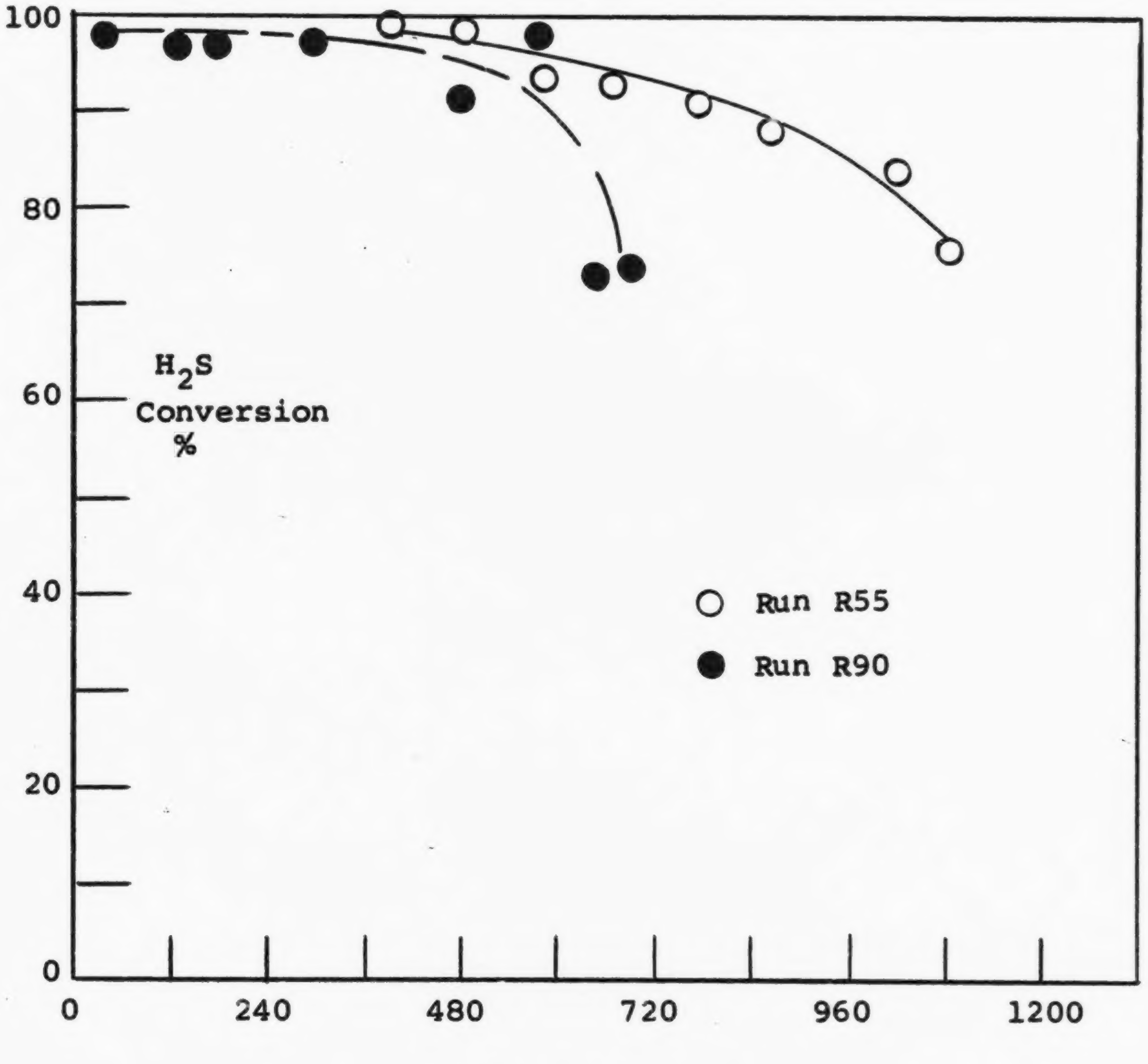
Note: (2) For stoichiometric feed ratios, theoretical yields based on CH_4 are for

$CH_4 + \frac{4}{x}S_x \longrightarrow CS_2 + 2H_2S$; CS_2-100%, H_2S-200%; and for

$CH_4 + \frac{4}{x}S_x + 2H_2O \longrightarrow CO_2 + 4H_2S$; CO_2-100%, H_2S-400%

FIGURE III-1: H_2S CONVERSION VS. TIME

Catalyst: Spence Actal A Activated Alumina
Temperature: 125°C
Space Velocity: 2900 std.vol./vol./hr.
Feed: 0.4% H_2S, 0.2% SO_2, 75 to 79% N_2, 3.3 to 5.7% H_2O, 3.5 to 4.5% O_2, 13 to 14% CO_2.



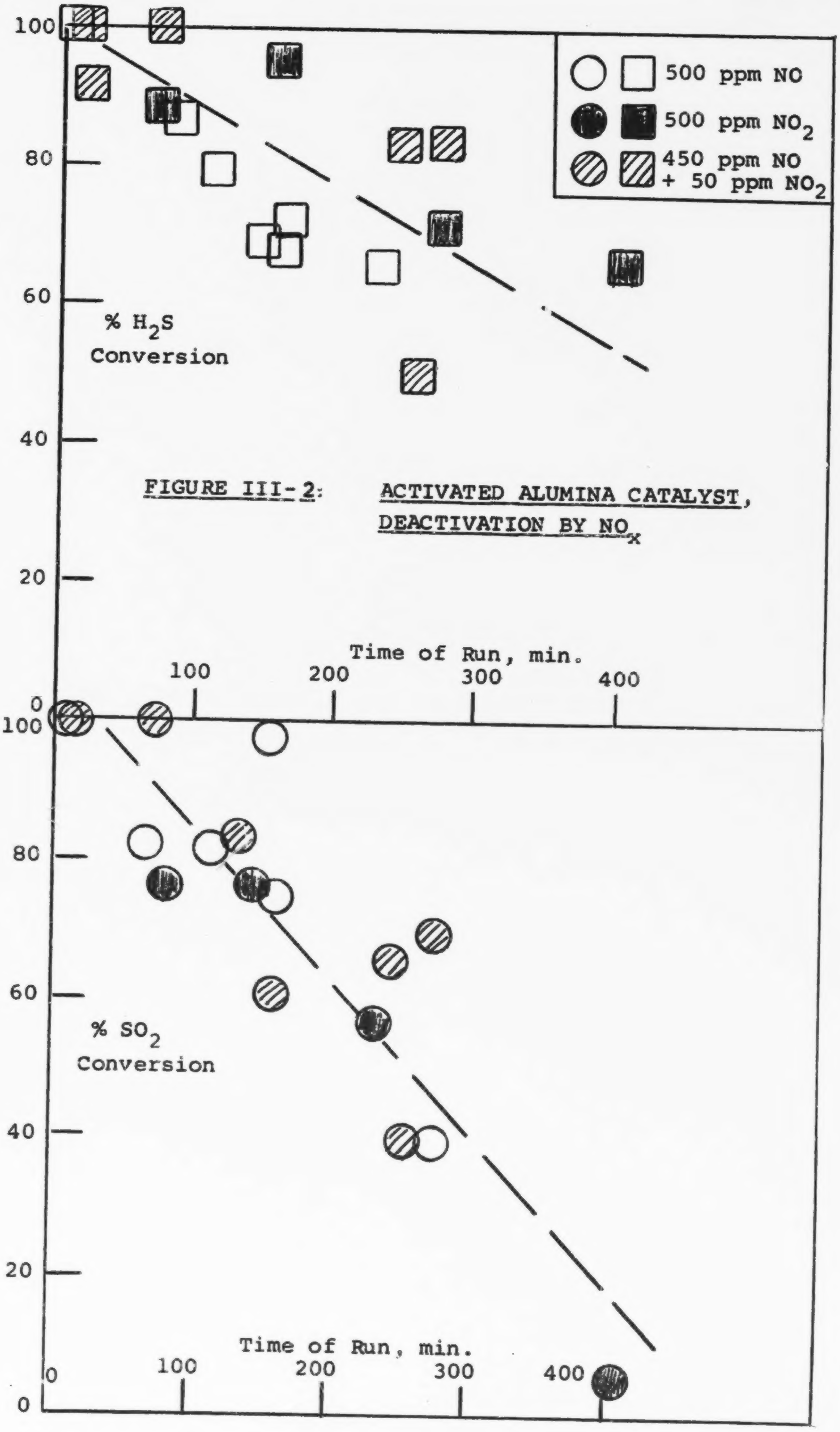


FIGURE III-2: ACTIVATED ALUMINA CATALYST, DEACTIVATION BY NO_x

FIGURE III-3: EFFECT OF INTERRUPTING NO_x ADDITION, ON SO_2 REDUCTION

MCB AX-610 Activated Alumina Catalyst

Reduction Temperature: 110°C

Feed: 0.4% H_2S, 0.2% SO_2, 75.9% N_2, 4.5% O_2,
14.0% CO_2, 5.0% H_2O

Space Velocity: 2620 std.vol./vol./hr.

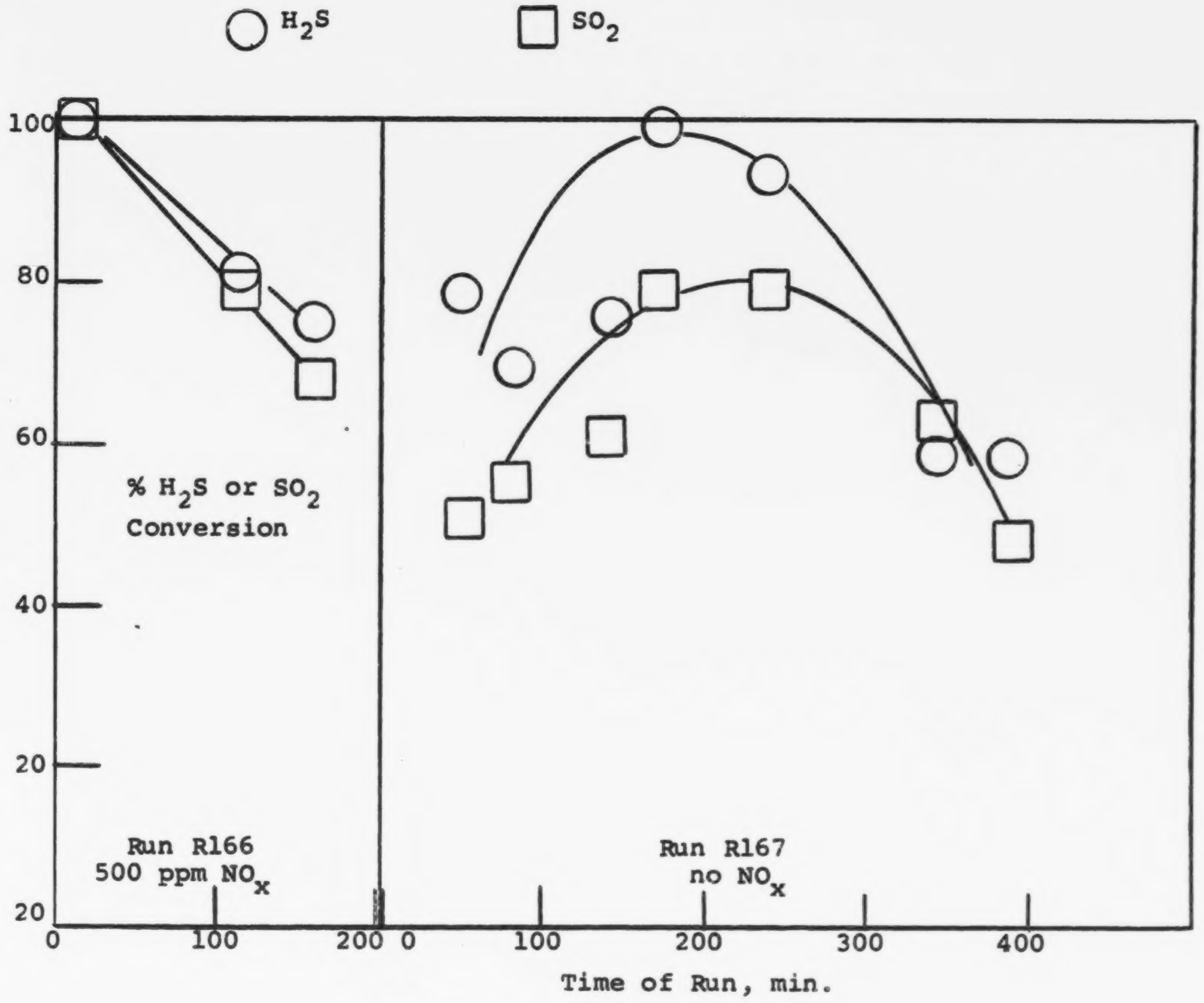
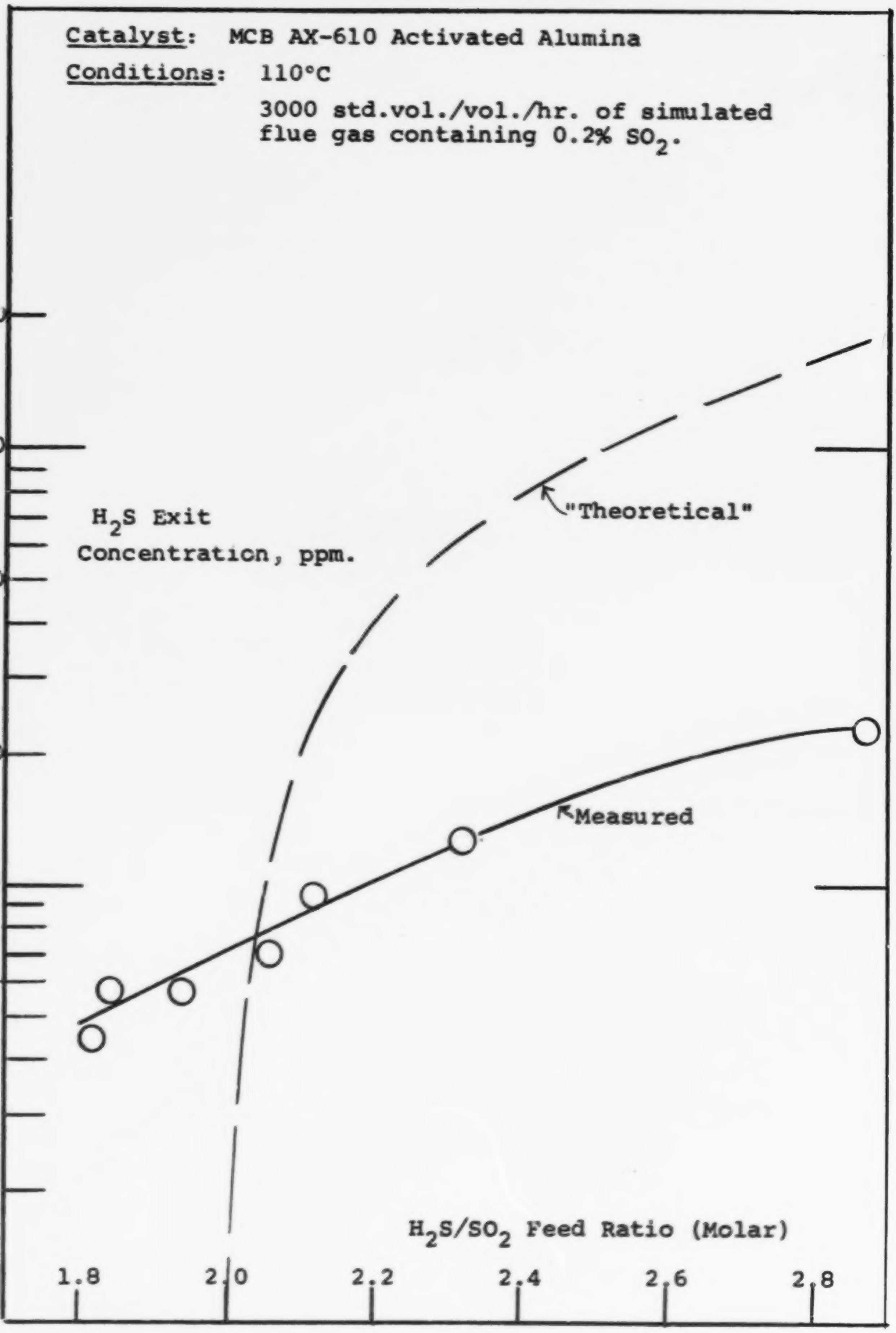


FIGURE III-4: H_2S EMISSION CONTROL: EFFECT OF H_2S/SO_2 FEED RATIO ON H_2S EXIT CONCENTRATION



Catalyst: MCB AX-610 Activated Alumina

Conditions: 110°C

3000 std.vol./vol./hr. of simulated flue gas containing 0.2% SO_2.

FIGURE III-5: RUN R76: H_2S CONVERSION VS. TIME

Catalyst: Linde Molecular Sieve 13X, 10-20 mesh
Temperature: 110°C
Space Velocity: 2620 std.vol./vol./hr.
Feed: Simulated flue gas composition containing
0.2% SO_2, 450 ppm NO, 50 ppm NO_2.

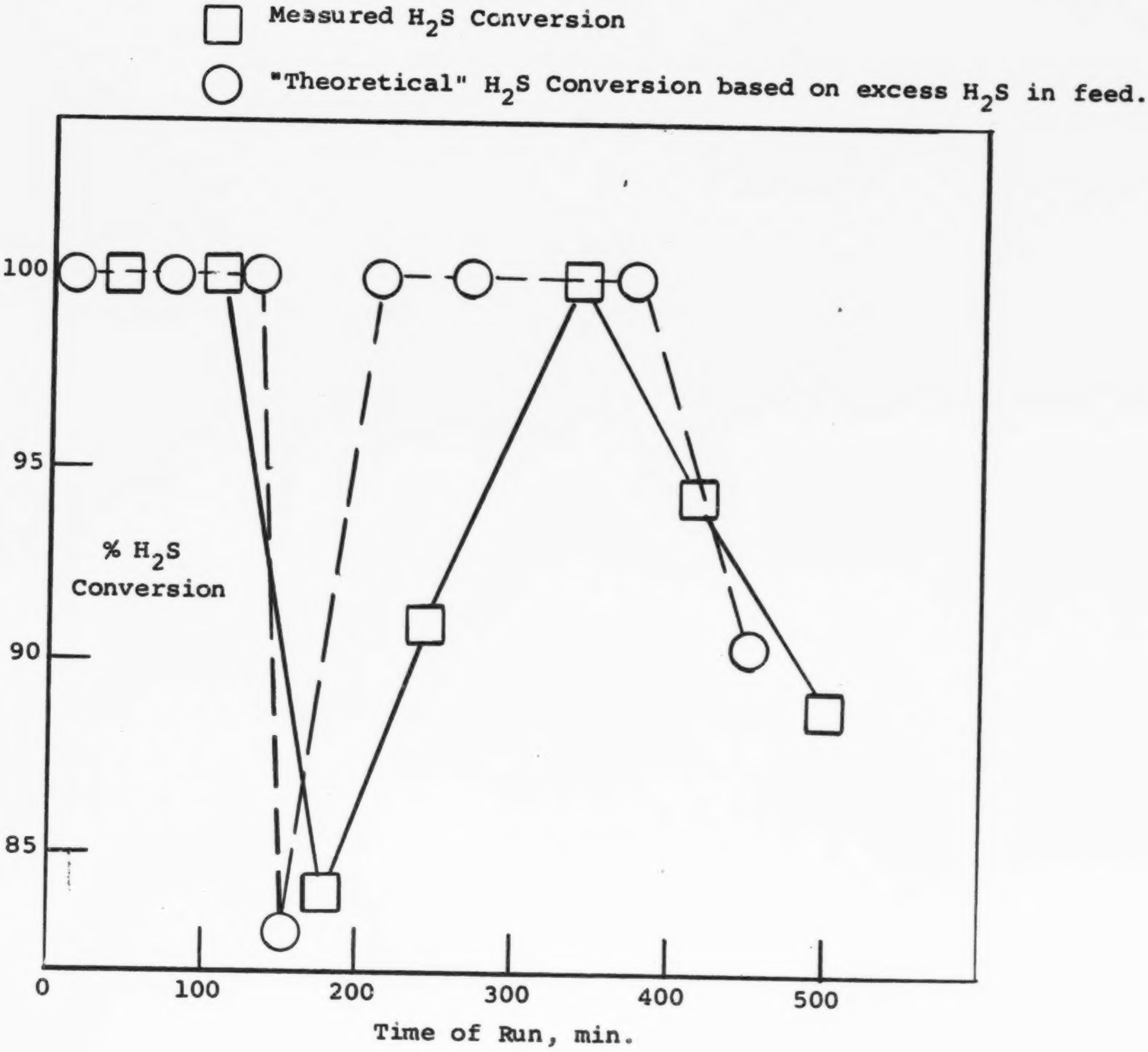


FIGURE III - 6. SULFUR DIOXIDE REDUCTION ASSEMBLY No. 1

KEY:

CF: capillary flowmeter
M: mercury manometer
MC: mixing coil
NV: needle valve
PG: pressure gage
R: rotameter
SP: sampling point
===:heating tape

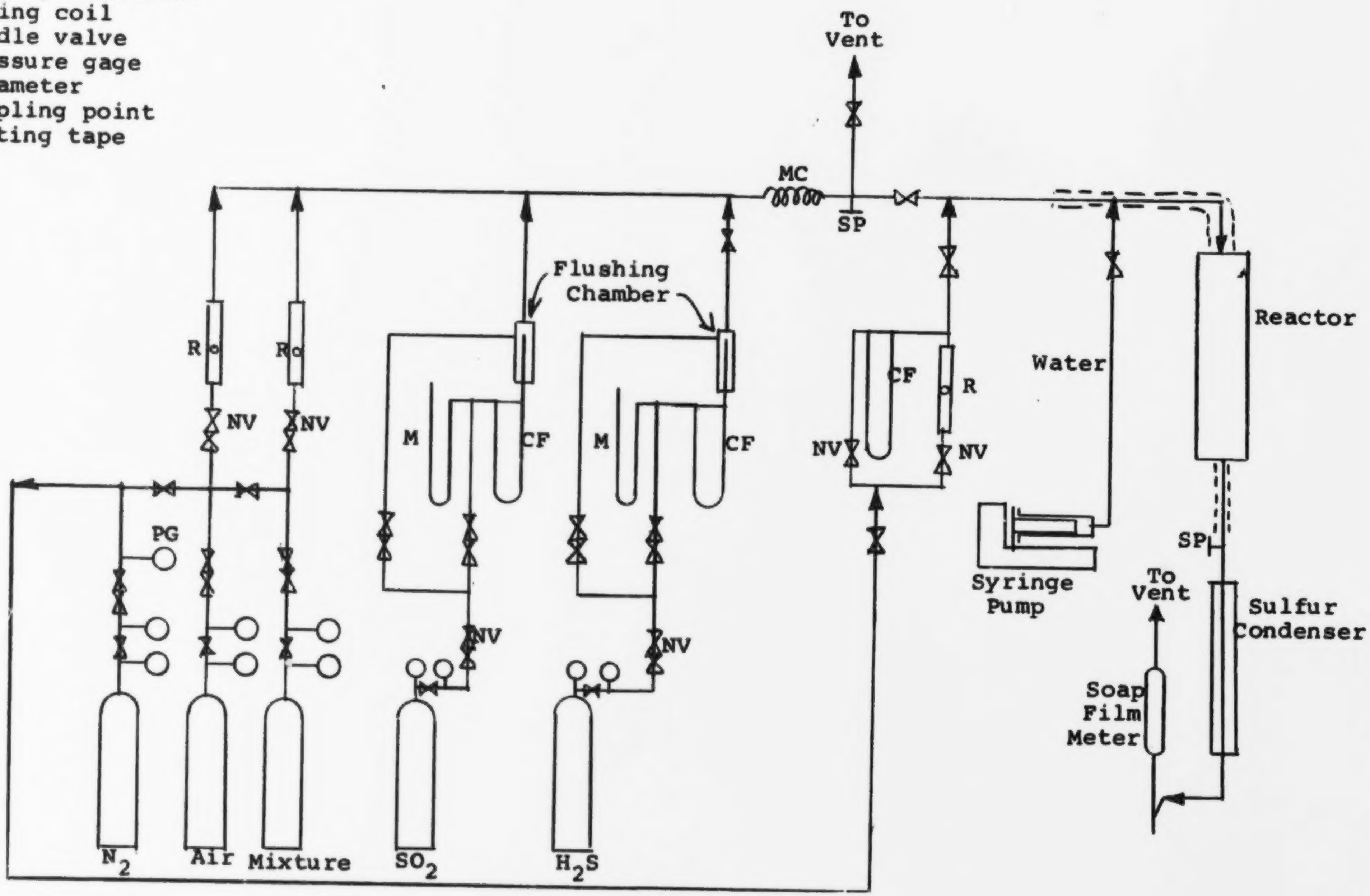
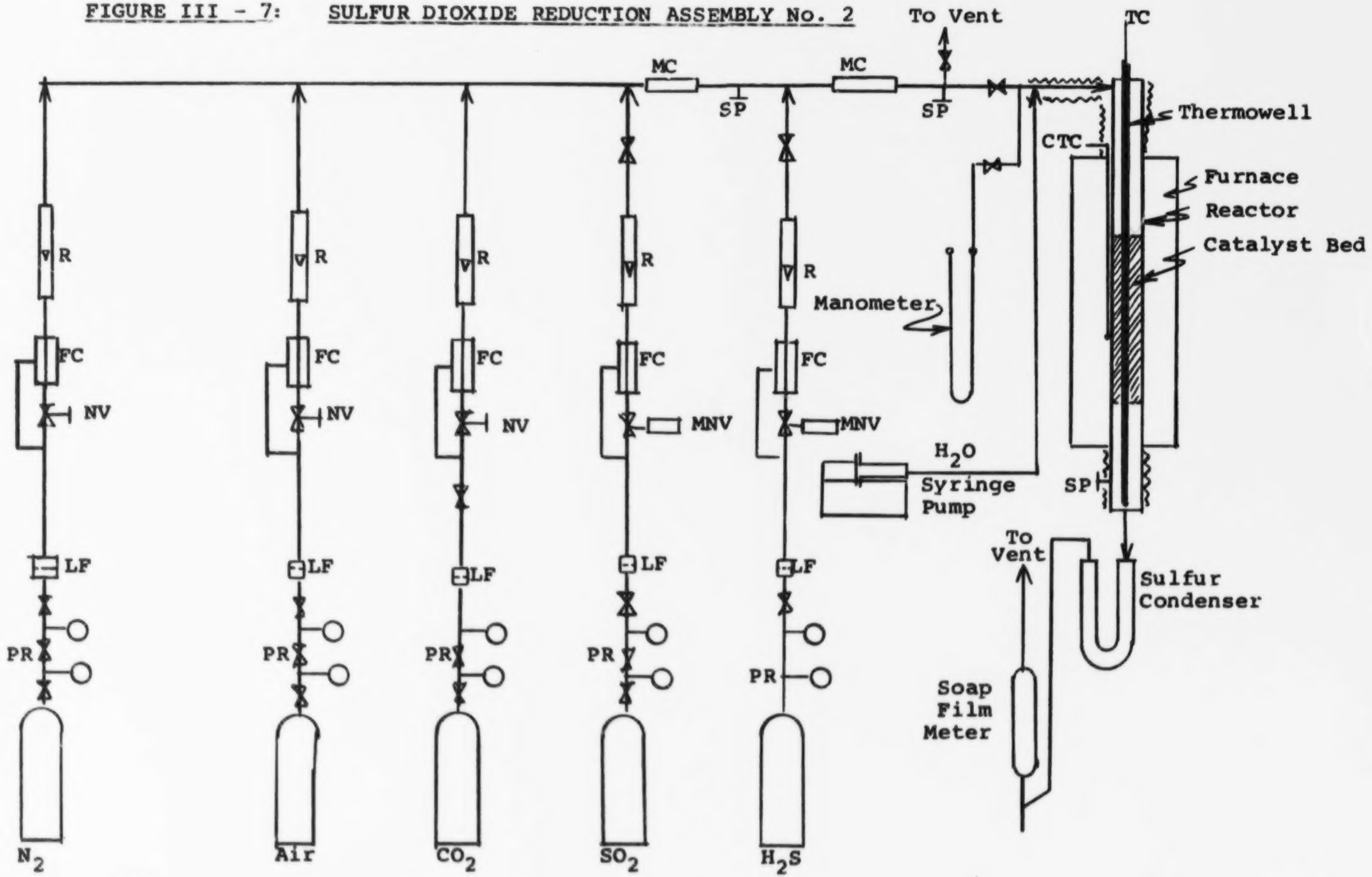

To Vent
MC
SP
Flushing Chamber
R
NV
PG
M
CF
Water
Reactor
Syringe Pump
To Vent
SP
Sulfur Condenser
Soap Film Meter
N₂
Air
Mixture
SO₂
H₂S

FIGURE III - 7: SULFUR DIOXIDE REDUCTION ASSEMBLY No. 2

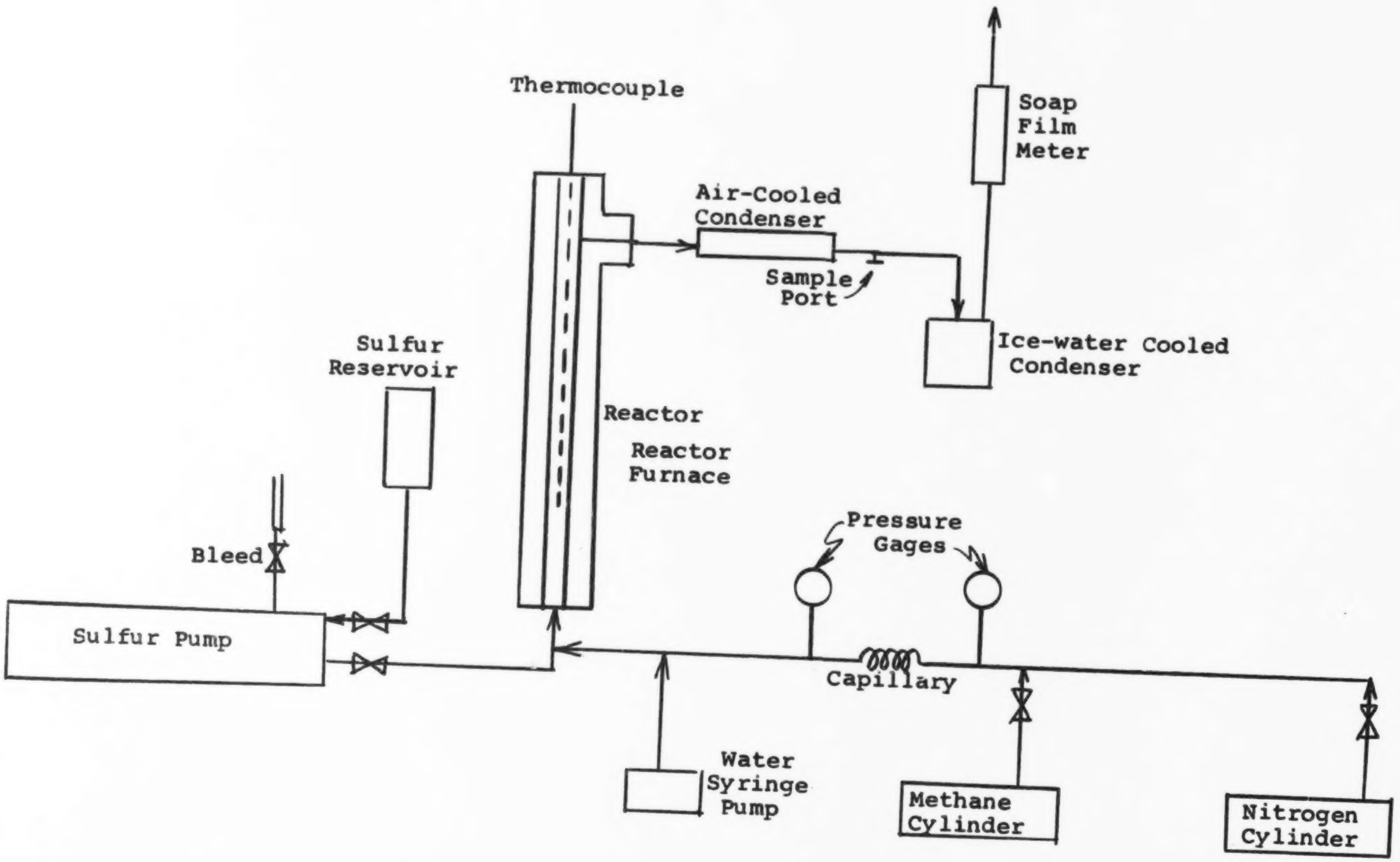

To Vent
TC
MC
SP
MC
SP
Thermowell
CTC
Furnace
Reactor
Catalyst Bed
R
FC
NV
MNV
LF
PR
Manometer
H_2O
Syringe Pump
SP
To Vent
Sulfur Condenser
Soap Film Meter
N_2
Air
CO_2
SO_2
H_2S

KEY:

CTC: controlling thermocouple
FC: flow controller
LF: line filter
MC: mixing tube
MNV: micrometer needle valve
NV: needle valve

PR: pressure regulator
R: rotameter
SP: sampling point
TC: readout thermocouple
〰: heating tape

FIGURE III - 8: LABORATORY HYDROGEN SULFIDE GENERATION ASSEMBLY


Thermocouple
Soap Film Meter
Air-Cooled Condenser
Sample Port
Ice-water Cooled Condenser
Sulfur Reservoir
Reactor
Reactor Furnace
Pressure Gages
Bleed
Sulfur Pump
Capillary
Water Syringe Pump
Methane Cylinder
Nitrogen Cylinder

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION IV

PILOT PLANT

TABLE OF CONTENTS

SECTION IV - PILOT PLANT

Page

1. Pilot Plant Design and Construction 110

  1.1 Design Bases 110

    1.11 Flue Gas Generation 111
    1.12 SO_2 Reduction 112
    1.13 Sulfur Stripping and Recovery and Catalyst Regeneration 112
    1.14 H_2S Generation 113

  1.2 Specifications and Construction 113

    1.21 Flue Gas Generation 113
    1.22 SO_2 Reduction 115
    1.23 Sulfur Stripping and Recovery and Catalyst Regeneration 115
    1.24 H_2S Generation 117
    1.25 Auxiliary Systems 118

2. Pilot Plant Results 119

  2.1 SO_2 Reduction 119

  2.2 H_2S Generation 121

LIST OF TABLES

SECTION IV - PILOT PLANT

Table	Title	Page
IV-1	Pilot Plant Equipment List - Flue Gas Section	122
IV-2	Coal Combustor Modification Parts List	123
IV-3	Design Conditions - Natural Gas Booster	124
IV-4	Pilot Plant Equipment List - SO_2 Reduction Section	125
IV-5	Pilot Plant Equipment List - Sulfur Stripping and Recovery and Catalyst Regeneration	126
IV-6	Design Conditions for Stripping Gas Dryers	127
IV-7	Pilot Plant Equipment List - H_2S Generation Section	128
IV-8	Pilot Plant Equipment List - Auxiliary Systems	129
IV-9	Pilot Plant Operating Data - H_2 Generator	130
IV-10-16	Pilot Plant Operating Data - SO_2 Reduction, Alumina Catalyst	131
IV-17	Pilot Plant Operating Data - SO_2 Reduction, Molecular Sieve Catalyst	138

LIST OF FIGURES

SECTION IV - PILOT PLANT

Figure	Title	Page
IV-1	Pilot Plant Flow Scheme Block Diagram	140
IV-2	Pilot Plant Flowsheet	142
IV-3	Pilot Plant Combustor - Cooler Schematic	143
IV-4	Pilot Plant Combustor Cooler Original Piping and Wiring Diagram	144
IV-5	Combustor - Cooler General Assembly	145
IV-6	Flue Gas Cooler Details	146
IV-7	Coal Combustor Details	147
IV-8	Coal Burner General Assembly	148
IV-9	Coal Burner Details	149
IV-10	Flue Gas Generation Section Flowsheet	150
IV-11	Coal Burner and Controls Modifications	151
IV-12	Coal Feeder Engineering Drawing	152
IV-13	Natural Gas Booster Engineering Drawing	153
IV-14	SO_2 Reduction Section Flowsheet	154
IV-15	Sulfur Stripping and Recovery Section Flowsheet	155
IV-16	Stripping Gas Blower Engineering Drawing	156
IV-17	H_2S Generation Section Flowsheet	157
IV-18	Panel Board Layout	158

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION IV - PILOT PLANT

1. Pilot Plant Design and Construction

1.1 Design Bases

The pilot plant design criteria were chosen to achieve the following objectives:

(a) Operate the process on flue gas generated by the combustion of coal.

(b) Achieve scale-up and integration of various process steps.

(c) Determine effects of process variables.

(d) Test materials of construction.

(e) Produce significant quantities of sulfur.

To accomplish these objectives, the pilot plant would:

(a) Integrate all the process steps.

(b) Generate flue gas by the combustion of pulverized coal.

(c) Contain reducing reactors to accommodate large particle sizes which may be necessary for economic pressure drops. Allow for 1-8 foot catalyst bed depths.

(d) Consist of materials believed suitable for commercial installation.

(e) Contain sulfur recovery systems.

(f) Be instrumented for accurate and predictable variation of process parameters.

The pilot plant was designed to produce five pounds/day of sulfur based on 3% sulfur coal.

Figure IV-1 is a block diagram and projected material balance for the pilot plant. Figure IV-2 is a more detailed flow diagram.

1.11 Design Basis - Flue Gas Generation

The generation of typical flue gas for small scale piloting cannot be accomplished by simple coal burning equipment such as home heating stokers. Power stations are able to operate at 20% (or less) excess air because of the size of their equipment, but small stokers are not very efficient.

In a small stoker the coal burns in stages, and produces a flue gas of varying composition. Fly ash in the flue gas is low. Difficulty was expected in sealing a simple stoker to the small back pressure anticipated during operation. For these reasons, a pulverized coal burner was decided upon.

Although Bituminous Coal Research, Inc. (Pittsburgh) and others had worked on design and fabrication of small pulverized coal furnaces, the Bureau of Mines (Pittsburgh) appeared to have the most experience. A conference with them was very helpful, and led to the involvement of General Ionics (Bridgeville).

General Ionics had done some of BuMines fabrication, and was at the time fabricating a new BuMines pulverized coal furnace. General Ionics offered to build a similar one for PCR. This offer was accepted. The combustor was to be built subject to the following criteria:

(a) Capability of burning pulverized coal and/or natural gas.

(b) Capability of burning coal at the rate of 8 pounds per hour at 20% excess air, with some variability.

(c) Capability to withstand and operate at pressures of at least 5 psig.

(d) Stainless steel and refractory-brick construction.

(e) Adequate safety and control devices.

An integral cooler was to be provided to cool the flue gas to 300°F. Fly ash laydown was to be minimized.

The pulverized coal feeder was to be capable of feeding coal at a comparable rate, and against the back pressure of the downstream equipment.

Fly ash removal equipment of course had to be capable of removing a high percentage of the ash. Pilot scale precipitators were not available, so fabric filters were to be utilized. A cyclone would help reduce the load on the filters.

1.12 Design Basis - SO_2 Reduction

The economic evaluations indicated that switching fixed beds were the most promising reactor design for the reduction step. The reactor design had to be capable of:

(a) Providing the desired residence time (approximately two seconds) with some variability.

(b) Operating with large (perhaps one-inch pellets) catalyst particles (because of pressure drop concern) without large wall effects.

(c) Temperature cycling (200-1000°F)

(d) Easy switching

(e) Easy catalyst changing

(f) Withstanding 5 psig internal pressure.

Two vertical tubular reactors of 4" diameter x 10' height and wrapped with beaded electrical heating wire satisfied these criteria.

1.13 Sulfur Stripping + Recovery + Catalyst Regeneration Design Basis

Laboratory work and heat transfer calculations indicated that sulfur stripping and catalyst regeneration could be accomplished in the same length of time that a parallel reactor would go through a reduction cycle if the stripping gas flow rate was about one-third the flue gas rate, the stripping gas temperature at 900-1000°F, and the stripping gas composition 5% (volume) H_2S in nitrogen.

A closed system, where the sulfur would be carried from the catalyst by the gas, condensed and recovered, with the gas returning to the stripping, was necessary because of the large volumes of gas required. A compressor, heater, condenser, and gas dryer were specified. Materials of construction were carefully considered.

1.14 Design Basis - H_2S Generation

The H_2S generator commercially is expected to be an adiabatic fixed bed reactor. On a small pilot scale, adiabatic operation is very difficult to achieve. Although the reaction is exothermic, it was expected that heat losses would be greater than the heat of reaction. Therefore, heat input to the reactor would be necessary.

In addition to preheating capacity, the reactor would be jacketed with an electric tube furnace. The reactor itself was to be a vertical tube reactor and lined with refractory which would protect the shell from the highly corrosive environment.

Design bases included:

(a) 1300°F temperature.

(b) Pressures to 5 psig.

(c) Gas flow of 0.135 SCFM, outlet.

(d) Superficial Space Velocity of 300 vol/hr/vol.

1.2 Specifications and Construction

1.21 Specifications and Construction - Flue Gas Generation

This section of the pilot plant is best described by the following tables and figures:

Table IV-1 List of Major Equipment
Figure IV-3 Combustor-Cooler Schematic
IV-4 Combustor-Cooler Piping & Wiring Schematic
IV-5 Combustor-Cooler General Assembly

Figure IV-6 Flue Gas Cooler Details
IV-7 Coal Combustor Details
IV-8 Coal Burner General Assembly
IV-9 Coal Burner Details
IV-10 Flue Gas Generation Section Flowsheet

Because of the difficulties of operating the coal combustor, described in Section VII-2.3, modifications were made to the burner and controls and are outlined in Table IV-2 and Figure IV-11. These were primarily to convert the pilot ignition to an electrical system, to replace the burner and to provide more safety features in the control system. These were designed and provided by the North American Mfg. Co. (Cleveland).

The pulverized coal feeder chosen was a Vibra Screw (Totowa, N.J.) Live Bin Feeder. Equipped with a 5/8" screw, a three cubic foot hopper, and pressure equalization taps, the feeder had a range of approximately 2-20 lbs./hr. of pulverized coal. Figure IV-12 gives the pertinent dimensions and configuration.

Natural gas was required to preheat the furnace. Line pressure was not sufficient to overcome the projected system pressure drops, so a booster was required. A Roots Connersville (Connersville, Indiana) Type XA Rotary Positive Displacement Gas Pump, Size 315 was chosen. Since it was oversized, a bypass with cooler was included. Table IV-3 lists the specifications and expected performance. Figure IV-13 is a detailed drawing of the motor and gas pump.

Combustion air was supplied by metering (Fisher & Porter rotameters and Fisher Governor regulator) the appropriate quantities of air from the PCR compressed air system.

A Design 3, UOP cyclone was used as a primary fly ash separator. Two Stokes Model 900-322-2 filters were installed for secondary fly ash recovery.

1.22 Specifications and Construction - SO_2 Reduction

The main reactors were fabricated from four-inch Schedule 40 (4.026" i.d.) stainless steel pipe. One was Type 310, the other Type 446. Each was ten feet long, wrapped with electrical heating wire, and insulated. Manifolded with high temperature ball valves, the reactors could be switched from reduction to stripping in a few seconds. Each reactor was equipped with a manometer for pressure drop measurements.

The reactors had flanged ends (150 lb., 316 SS flanges) with one-inch pipe connections. Compressed asbestos gaskets were used. One-quarter inch, 316 SS tubing was inserted in the reactors axially as thermowells. Catalyst was supported by 6 mesh stainless steel wire screen at the bottom of the reactors.

Power to the electrical heating wires was supplied through 7.8 KVA, 240 volt powerstats (one for each reactor). Temperature control for reduction was maintained by a Honeywell Type 7160 electronic controller.

A fixed bed of Matthey Bishop (Malvern, Pa.) honeycomb platinized alumina catalyst was jacketed in a tube furnace to provide incineration of the H_2S in the flue gases during upset conditions.

Figure IV-14 is a flowsheet of the SO_2 reduction section. Table IV-4 is the equipment list.

1.23 Specifications and Construction - Sulfur Stripping and Recovery and Catalyst Regeneration

This section of the pilot plant is a recirculating system consisting of the following major equipment items:

(a) Stripping gas compressor

(b) Stripping gas heater

(c) Sulfur condenser

(d) Sulfur knock-out drum

(e) Stripping gas dryer

Figure IV-15 is a flowsheet of this section of the plant. Table IV-5 is a detailed list of the major equipment items and specifications.

The stripping gas compressor required was very small (500 SCFH, 10 psi Δp). A Gardner-Denver (Quincy, Illinois) Rotary Blower Model 2PDR4, available only in cast iron, was found to be the most suitable model on the market. The risk of utilizing the cast iron for the probably corrosive stripping gas was reluctantly taken. The blower was installed with a by-pass system for stripping gas flow control. Figure IV-16 is a print of this item.

The heat required for stripping was supplied by a Model GCH-6120WV Chromalox (Pittsburgh, Pa.) electric air heater, capable of heating 45 lbs./hour of nitrogen from 250-1000°F. The electric elements were of Incoloy with aluminum metallizing for high temperature resistance. The heater was equipped with a thermostat and a high temperature cut-off; rated at 3600 watts, it was powered by a 208 volt, 3 phase circuit. Piping from the heater to the reactors was traced with beaded heating wire to maintain temperatures.

Sulfur condensation was to be carried out in what was basically an air cooled (natural convection) condenser. Consisting of a 6" i.d. x 7.5 foot Pyrex glass pipe ~11 ft^2), the condenser was also jacketed with electric heating mantles (230 volt Glas Col) for temperature control and sulfur melt-out. It was expected that the condenser would cool the stripping gas to about 250°F, condensing sulfur as a non-viscous liquid which would run down the walls of the glass pipe. The mantles would help control the temperature in the sulfur flow region.

Expecting some sulfur carry-over from the condenser, a knock-out system was installed to collect it and moisture from the stripping gas. The system consisted of a thirty-gallon drum (where the gas velocity would drop enough to allow settling of sulfur particles) which had cooling coils (80 feet of 1/4" copper tubing) wrapped around it (to lower the gas temperature to condense any moisture).

Molecular sieve gas dryers were installed in case bone-dry stripping gas was required. Two 8" diameter x 36" pipes were wrapped with beaded wire heaters (for regeneration) and were packed with 4-8 mesh Davison (Baltimore) Type 3A molecular sieves. Table IV-6 lists the operating parameters for this system.

Stripping gas flow was controlled by rotameter. Nitrogen and H_2S make-up to the system was provided from gas bottles metered through rotameters. Humidity control was provided by a Milton Roy (St. Petersburg, Florida) Mini-Pump. (0-300 ml/hr)

1.24 Specifications and Construction - H_2S Generation

Table IV-7 lists the major equipment items of this section of the plant. Figure IV-17 is a flowsheet of the section. It consists of the following items:

(a) H_2S generator reactor

(b) Sulfur feed pump

(c) Water feed pump

(d) Sulfur vaporizer

(e) Sulfur disentraining pot

The reactor is a fixed bed tubular reactor. It was fabricated from a three-foot length of two-inch Schedule 40 Type 310 stainless steel pipe. A 1-5/8 inch i.d. Mullite sleeve was inserted into the pipe and bonded in place with acid resistant refractory cement. The ends of the reactor were fitted with standard 150 lb. slip-on flanges of 316 S.S. Flanged connections were used to connect 3/4 inch inlet and outlet piping. Compressed asbestos gaskets were used.

A 1/4" o.d. 316 S.S. thermowell was inserted axially. The catalyst was loaded in the annulus between the Mullite and the thermowell and was supported by a stainless steel screen at the bottom of the reactor.

The whole reactor assembly was inserted in a 2-1/2" i.d. Hevi-Duty (Lindberg Hevi-Duty, Chicago, Ill.) tube furnace for temperature control.

Molten sulfur was fed to the reactor by a jacketed piston pump, BIF (Providence, Rhode Island) Micro Feeder Code 1180-20. This pump provided pulsationless feeding of the molten sulfur at any pressure (rated up to 1000 psi).

A Fluid Metering (Oyster Bay, N. Y.) pump RRP2G20 had been tried previously (with tracing for temperature control). It did not function well because of temperature control difficulties.

The sulfur vaporizer consisted of a twelve-inch length of 3/4 inch Schedule 40 pipe jacketed with a one-inch Hevi-Duty tube furnace. Electrical tracing was used on piping between the vaporizer and the reactor to prevent sulfur condensation.

Water was fed to the system by a Milton-Roy Mini Pump #1B29R (0-300 ml/hr). Natural gas was metered through a Fisher and Porter rotameter from the natural gas booster (Flue Gas Section). Both were preheated in traced feedlines and in the lower section of the reactor.

Downstream of the reactor was mounted a 5" i.d. x 2-foot vertical pipe where the unreacted sulfur was condensed and collected.

1.25 Specifications & Construction - Auxiliary Systems

To maintain the temperature of sulfur between its freezing point and high viscosity temperature, a hot oil tracing system was installed. Table IV-8 lists all the pertinent statistics of the system.

Table IV-8 also details the catalytic incinerator (previously described) and the main air compressors.

Figure IV-18 is the panel board layout. All the important process temperatures, pressures, and flows are indicated, recorded, and/or controlled from this board. In addition, the oxygen concentration of the flue gas is continuously indicated by an oxygen monitor (Beckman Model 714, 0-25% oxygen).

2. Pilot Plant Results

2.1 SO_2 Reduction

Scale-up of the SO_2 reduction step was inconclusive and requires further work. With the alumina catalyst, the following experimental conditions were run (See Tables IV-10, 11, 12, 13, 14, 15, 16).

Flue Gas	Source of H_2S	Source of SO_2	Range of Space Velocity V/V/HR	Temperature °F
Air	H_2S Generator	Gas Bottles	1000-2000	248-257
Combustion of Coal	H_2S Generator	Sulfur in Coal	2300-2900	212-260
Combustion of Coal	Gas Bottles	Sulfur in Coal	2000-2800	212-239
Combustion of Coal	Gas Bottles	Sulfur in Coal	1100-1600	203-275
Combustion of Natural Gas	Gas Bottles	Gas Bottles	1100-2100	176-221
Combustion of Natural Gas	Gas Bottles	Gas Bottles	1900	212
Combustion of Natural Gas	Gas Bottles	Gas Bottles	1600	203-230

With the 13X molecular sieve, the following conditions were run (See Table IV-17):

Combustion of Natural Gas With Bottled NO_x added	Gas Bottles	Gas Bottles	1500	212

All of these experiments resulted in poor initial conversions or a continuous decline of a high initial conversion.

Several reasons may have possibly contributed to this result:

(a) Insufficient data and operating time

- Severe delays in delivery and start-up of the coal combustor reduced the operating time from a projected seven months to slightly more than two months.
- Most of the work was done with activated alumina, later found to be very affected by nitrogen oxides.
- Molecular sieves were tried for only one week, not a long enough period of time to gather meaningful data.
- The catalyst stripping and regeneration system was not studied adequately during operation and may not have been functioning as expected.

(b) Major differences between bench and pilot plant

- Larger catalyst particles were used
- Combustion flue gases were used and certainly contained at least traces of extraneous materials such as fly ash, SO_3, and unburned hydrocarbons, effects of which were not studied at the bench.
- Higher linear velocities were used in the pilot plant even though space velocities were the same.

Pilot plant operating data are required for a prototype plant design. Effects of catalyst size, space velocity, temperature, and linear gas velocity must be determined. Sulfur stripping and recovery conditions must be optimized. Catalyst life expectancy must be developed. Pressure drop measurements must be made over a reasonably long time period. Further pilot planting is required.

2.2 H_2S Generation

The H_2S generation step was studied very little in the pilot plant. In the short period it was studied, successful scale-up was achieved. Better yields were obtained in the pilot plant, although the residence time was somewhat higher than the bench work.

Table IV-9 summarizes the data obtained in the pilot plant.

TABLE IV-1

PILOT PLANT EQUIPMENT LIST - FLUE GAS SECTION

Unit	Description	Special Features	Design		Materials of Construction
			Temp., °F	Press. psig	
Flue Gas Section					
Combustor-Cooler	By Ionics General Div. of Ionics Inc. Burns coal or natural gas in a 16" diam. x 45" long vertical chamber. 125,000 BTU/hr. Gas burner and controls modified by North American Mfg. Co.	Purge (air) control and flame sensing control provide positive control of gas valve.	3200 (Combustion Section)	5	Refractory lined steel
	Cooler section is a horizontal 16" diam. x 60" long air-cooled pipe attached to the lower (outlet) end of the combustor. 3/4 HP drive for cooling air fan.	Pressure control of cooling air fan will not permit gas firing unless fan is on. Alarm lights on cooling air fan and flue gas outlet pressure. Rupture disk at flue gas outlet set for 6.7 psig.	1500 (Cooler Section)	5	mild steel
Cyclone (fly ash) separator	Aerotic Div. of UOP. 3" diam., 2" inlet and outlet connections	Provides 90% removal of 5μ particles at operating conditions used.	-	>5	316 S.S.
Line Filters (2) (fly ash)	Stokes Model 900-322-2 2" inlet and outlet conns.	Rated for 70 cfm with 1μ retention	-	15	mild steel
Natural Gas Booster Pump	Roots-Connersville 315 Type XA gas pump; 7.5 cfm	2 HP, 1750 RPM driver. Pump equipped with recycle cooler and pressure regulator.	68	2-7	cast iron
Pulverized Coal feeder	Vibrascrew live bin feeder. 2 to 20 lbs./hr.	5/8" open helix screw. 100 lb. hopper capacity. 1/3 HP drive.	Amb.	6	cast iron

THE NORTH AMERICAN MFG. CO.
DISTRICT OFFICE WATCHUNG
DR. BY JP DATE 7/13/70

LEGEND
FOR
PRESSURE VESSEL

DISTRICT OFFICE NO. H-G17469-1
REVISED

ITEM NO.	DESCRIPTION
1.	#65-2-12 (1¼") mixer with #4025M-2 (1½") pilot tip
2.	#4065 ignition transformer
3.	#4085 ignition cable
4.	#8735-H (0 - 32 osi) air pressure gauge
5.	#PG-3 Range P1 (1 - 17 osi) purge proving switch
6.	#1125-2 (1¼") manual butterfly air valve
7.	#PG-3 Range P1 (1 - 17 osi) low air pressure switch
8.	#7347-23 (1¼") regulator
9.	#7218-0 (3/4") regulator
10.	#22-0-MS (3/4") manual reset rafety shutoff valve
11.	#8735-G (0 - 32 osi) gas pressure gauge
12.	#PG-3 Range P1 (1 - 17 osi) low gas pressure switch
13.	#1824-01 (½") valve
14.	#7345-01 (½") regulator
15.	#RA890-G Protectorelay
16.	#C7027A1023 ultraviolet detector
17.	#2412-AG Agastat purge timer (1 - 20 minutes)

TABLE IV-2

COAL COMBUSTOR MODIFICATIONS PARTS LIST

Refers to Figure IV-11

ROOTS
CONNERSVILLE
DIVISION OF DRESSER INDUSTRIES
900 WEST MOUNT STREET
CONNERSVILLE, INDIANA 47331

TABLE IV-3
DESIGN CONDITIONS
NATURAL GAS BOOSTER

Quotation No: 8-1201-05260

Dated August 12, 1968

at

Quotation To:

PRINCETON CHEMICAL RESEARCH CORP.
P.O. BOX 632
Princeton, N. J. 08540

Attn: Mr. Richard Toro

Subject GAS BOOSTER

We (the Manufacturers) propose to furnish the following apparatus at the prices, terms, and conditions named herein.

(1) Size 315 Type XA Rotary Positive Displacement Gas Pump
complete with the following:

(1) Relief Valve Regulator 1¼" Y611
( ) Inlet muffler filter
( ) Discharge silencer
(1) Cooler 303 HCF
(1) Clipper seals

1) Extended Baseplate
( ) V-belt drive
( ) V-belt guard
(1) Coupling and guard

EXPECTED PERFORMANCE:

Gas handled	Nat. gas S.G. 0.67
Inlet volume	7.5 CFM
Inlet temperature	68° F
Inlet Pressure	1 PSIG
Discharge pressure	7 PSIG
Speed	1750
BHP required	1.55

PRICE EACH .... $ 671.00

Approximate shipping weight: 300#

ADDITIONS

(1) 2 HP. 1750 RPM 3/60/230/460 TEFC Induction motor with slide rails, mounted on above baseplate.

PRICE EACH .... $ INC.

In order to meet your turn down requirement and to meet the design parameters of the pump, we must over pump and utilize bypass.

Prices specified herein for apparatus manufactured by Roots-Connersville are firm. Prices on purchased equipment will be adjusted to our supplier's price in effect at the time of shipment.

Shipment 7 - 8 Wks.

F.O.B. POINT OF MANUFACTURE

Accepted JK/rk 19

By

This quotation is subject to immediate acceptance. Any order resulting therefrom does not constitute a contract until approved by the Company at its executive offices.

Terms NET CASH 30 DAYS

ROOTS CONNERSVILLE

John Kash
By John Kash, District Engr.

Printed in U.S.A.

(CONDITIONS OVER)

Form No. SA-102Q 5M-1165

TABLE IV-4

PILOT PLANT EQUIPMENT LIST - SO_2 REDUCTION SECTION

Unit	Description	Special Features	Design Temp., °F	Design Press. psig	Materials of Construction
SO_2 reactors (2)	4.026" i.d. x 10 ft. long vertical reactors. Flanged to provide 1" gas inlet and outlet. Axial thermowell 1/4" o.d. tubing. Upflow during reaction. Downflow during sulfur stripping.	Wrapped with beaded nichrome wire and insulated to provide temperature control. 3½" high perforated catalyst support grid at lower end. Catalyst volume when full = 0.8 cu.ft. Fitted with 8 1" ball valves for switching gas flows (graphitar seats permit operation to 1000°F)	1000	15	Type 310 (one unit) Type 446 (other unit)

TABLE IV-5

PILOT PLANT EQUIPMENT LIST

SULFUR STRIPPING, RECOVERY AND CATALYST REGENERATION SECTION

Unit	Description	Special Features	Design Temp., °F	Design Press. psig	Materials of Construction
Stripping gas compressor	Gardner-Denver 2PDR4; 8.3 cfm rotary blower	3 HP, 1230 RPM driver	Suction: 150 Discharge: 275	5 (or 0) 15 (or 10)	Cast iron
Stripping gas heater	Chromalox Circulation heater GCH-6120 WV 4.8 KW, 208V, 3 phase	Self-contained thermostat MF2 and high limit indicator-control. Installed upstream of SO_2 reactor being stripped.	Suction: 250 Discharge: 1000 (45 lb./hr. N_2)	10	Incoloy with aluminum metallizing
Sulfur Condenser	6" i.d. x 7.5 ft. long Pyrex pipe with 1/4" o.d. axial thermowell. (Upflow)	Heating mantles permit melting of sulfur from the walls during off-cycle. Mantles act as insulation to prevent excessive heat loss during stripping.	500	5	Pyrex glass (resistant to thermal shock)
Sulfur knock-out drum	55 gallon steel drum fitted with 1" inlet and outlet conns. and 1/2" drain.	Fitted with external cooling coils to remove moisture and aid in condensation of sulfur carried over from sulfur condenser. Fiberglass insulated.	300	5	Mild steel Heresite lined.
Stripping gas dryers	8" i.d. x 3 ft. long vertical vessels with 1" inlet and outlet conns. Axial thermowell, 1/4" o.d. tubing. Downflow during drying cycle. Upflow during regeneration (with heated air).	Wrapped with beaded nichrome wire and insulated. Screen inserted above bottom flange to support molecular sieve charge. Fitted with 8 1" ball valves for switching gas flows. Stripping gas leaving dryers is recycled to stripping gas compressor.	500	5	316 S.S.

W. R. GRACE & CO.
DAVISON CHEMICAL DIVISION

TABLE IV - 6

DESIGN CONDITIONS FOR STRIPPING GAS DRYERS

Case II

		Composition
Conditions:		
Flow Rate	45 lb/hr.	N_2
	.02 lb/hr.	S
Pressure	0 psig	
Temperature	150°F	
Water Content	.1 lb/hr.	
Requirements	-80°F Dew Point	
Recommendations:		
Adsorbent	Davison Molecular Sieves, Grade 562	
Pore Size	3A°	
Particle Size	4-8 mesh	
Number of Vessels	2	
Adsorbent Quantity per Vessel	32 lbs.	
Bed Dimensions:		
Diameter	8 inches	
Height	2 ft.	
Cycle Time	8 hours	
Regeneration Temperature (Exit of Bed)	425°F Maximum	
Regeneration Gas Rate	70 lbs/hr. air at 450°F or 35 lbs/hr. Nat. Gas at 450°F	~17 SCFM
Direction of Flow:		
Treating	8 hours Down	
Heating	5 hours Up	
Cooling	3 hours Up	

Date: October 10, 1968

Milton F Potter

Milton F. Potter

MFP/mh

TABLE IV-7

PILOT PLANT EQUIPMENT LIST

H_2S GENERATION SECTION

Unit	Description	Special Features	Design Temp., °F	Design Press. psig	Materials of Construction
H_2S Generator	1-5/8" i.d. x 3 ft. long vertical reactor. (upflow)	Reactor mounted in 2½" i.d. Hevi-Duty furnace rated at 2.8 KVA. Lower section (7½") is packed with inert 1/8" tabular alumina balls for preheating the entering gas. Upper section will hold 950 cc's of catalyst when full.	1300	10	1-5/8" i.d. Mullite (refractory) tube bonded inside 2.067 i.d. type 310 S.S. pipe
Sulfur Vaporizer	0.824" i.d. x 12" long horizontal heated pipe.	Pipe is mounted in 1" i.d. Hevi-Duty furnace rated at 0.6 KVA.	1300	10	316 S.S.
Mixing Tee	0.824" i.d. x about 6" long	Sulfur vapor from sulfur vaporizer enters the horizontal connection. Flow is vertically upward leaving the tee where natural gas and steam are added. Tee is wrapped with beaded nichrome wire and insulated.	1300	10	316 S.S.
Sulfur Disentraining Pot	5" i.d. x 2 ft. long vertical pipe	Product gas leaving H_2S generator enters the top of the pot and leaves at the side. Gas is cooled and velocity is reduced drastically to disengage droplets of unreacted sulfur. Hot oil traced and insulated.	300	10	316 S.S.
Sulfur Feed Pump	BIF Proportioneers Adjust-O-Feeder Code 1180-20	Piston pump of approx. 1000 ml. cylinder capacity. Feed rate adjustable 0-750 ml./hr. jacketed.	300+	1000	316 S.S.
Water Feed Pump	Milton Roy Mini Pump #1B29R	Positive displacement pump, adjustable 0-300 ml./hr.	Amb.	100+	316 S.S.

TABLE IV-8

PILOT PLANT EQUIPMENT LIST

AUXILIARY SYSTEMS

Unit	Description	Special Features	Design		Materials of Construction
			Temp., °F	Press., psig	
Hot Oil Tank	55 gallon steel drum, connections for electrical heating units and for re-circulating oil	Vented tank, insulated. Pump suction conn. located on wall near bottom. Oil return conn. located on wall near top. Dial thermometer conn. near mid point of wall. 2 2.5 KVA electrical heaters mounted in 2 2½" connections in side wall of drum.	300	Atm.	mild steel-Heresite lined.
Hot Oil Re-circulation pump	Worthington 3/4 CNF 42 centrifugal pump. 20 gpm at 70 ft. discharge head.	3/4 HP driver.	300	-	Cast iron
Catalytic Incinerator	3" o.d. x 30" vertical tube	Holds 2 honeycomb-type catalyst cylinders approximately 12" long. Mounted in 3" i.d. Hevi-Duty tube furnace rated at 3.4 KVA.	1000	Atm.	316 S.S.
Plant Air Compressor (Main)	Worthington, Model 15T-2	Size: 6/3½ x 2-3/4; 15 HP driver. 50 SCFM rated capacity.	Amb.	150	Cast iron
Plant Air Compressor (Auxiliary)	Ingersoll-Rand, Type 30	Size: 5/3 x 3½; 5 HP driver 20 SCFM rated capacity.	Amb.	150	Cast iron

----

Process Control Instruments: Various electronic temperature controllers - Honeywell, Thermo-Electric, Leeds & Northrup.
Self regulating pressure controllers - North American Mfg. Co., Fisher Governor Co.
Rotameters - Fischer and Porter, Brooks, Matheson.
Oxygen Monitor - Beckman Model 715

TABLE IV-9

PILOT PLANT OPERATING DATA

H_2S GENERATOR

Date	Time	Reactant Feed Rates, Gm.Moles/Hr.			Feed Ratio	PROCESS DATA			
						Reactor		Gas Flow Rate,(1)	Space Velocity
		Sulfur	Water	CH_4	$S/H_2O/CH_4$	Temp., °F	Press.Psig	Std.l./hr.	Std.V./V./Hr.(2)
3/19	~10:00AM	6.35	9.30	2.49	3.7/2.6/1.0	1330	-	245	301
4/2	3:25PM	7.04	4.56	1.49	4.7/3.1/1.0	950	2.0	175	216
4/9	5:30AM	7.24	4.00	1.54	4.7/2.6/1.0	1325	2.5	171	211
4/18	6:15AM	7.07	4.55	1.51	4.7/3.0/1.0	1320	3.0	183	225
4/22	9.10AM	6.90	5.57	1.81	3.8/3.1/1.0	1340	4.0	214	264

		Product Gas Composition, Mole %						Conversion, Mole %			Material Balance, %		
Date	Time	CO	CH_4	CO_2	H_2S	H_2O	COS	S	H_2O	CH_4	H(3)	S	C
3/19	~10:00AM	0.17	0.11	17.86	73.64	7.43	0.79	110	84	100	100	110	101
4/2	3:25PM	2.81	5.28	17.45	61.05	12.54	0.88	78	75	69	100	78	136
4/9	5:30AM	0.05	--	17.30	15.70	22.80	0.13	71	51	100	100	71	96
4/18	6:15AM	0.30	2.90	17.40	70.00	8.70	0.60	89	83	83	100	89	120
4/22	9:10AM	0.71	4.08	18.15	76.10	--	0.96	120	100	75	100	120	134

Notes:

(1) Standard conditions are defined as 70°F and 1 atm. pressure

(2) Catalyst volume = 810 cc's

(3) Hydrogen balance was assumed equal to 100%

TABLE IV-10

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst: -3/8 + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume

Space Velocity: 960-2010 std. vol./vol./hr.

Flue Gas: (a) Combustion of natural gas; (b) air

Source of H_2S: H_2S generator (see Table IV-9)

Source of SO_2: Gas bottles

Date	Time	Flue Gas	Hours on stream(1)	Flue Gas Total(2) GMPH	V/V/Hr.	%H_2S	%SO_2	H_2S/SO_2	Temp., °F
3/19	~10:00 AM	(b)	-	565	960	1.32	0.47	2.81	~250
4/2	2:15 PM	(a)	10	992	1680	0.55	0.47	1.18	257
4/9	2:10 AM	(b)	1.7	1185	2010	0.47	0.30	1.57	248
4/18	2:20 PM	(b)	4.3	1120	1900	0.56	0.29	1.92	257
4/18	8:15 AM	(b)	8.2	1120	1900	0.56	0.29	1.92	257
4/22	10:10 AM	(b)	2.2	1117	1900	0.74	0.31	2.43	248

		Product Gas Composition, Mole %					Conversion Mole %		Material Balance, %			
Date	Time	N_2+O_2	CO_2	H_2S	H_2O	SO_2	H_2S	SO_2	H	O	C	S
3/19	~10:00 AM	98.8	0.28	0.21	0.55	0.14	84	71	46	70	77	-
4/2	12:10 PM	91.4	7.62	0.17	0.64	0.15	69	68	69	97	97	-
4/9	2:10 AM	98.7	0.07	0.14	0.26	0.81	71	--	61	157	42	-
4/18	2:20 PM	98.9	0.20	0.25	0.60	0.05	56	83	72	80	65	-
4/18	8:15 AM	99.1	0.10	0.20	0.30	0.22	64	26	39	68	32	-
4/22	10:10 AM	99.7	0.10	0.00	0.00	0.13	100	57	--	23	27	-

(1) After sulfur stripping and catalyst regeneration (2) Gram - Moles per hour

TABLE IV-11

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst:	-3/8 + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume
Space Velocity:	2350-2850 std. vol./vol./hr.
Flue Gas:	Combustion of pulverized coal
Source of H_2S:	H_2S Generator
Source of SO_2:	Sulfur in coal

Date	Time	Hours on Stream	Flue Gas				
			Total Gm Moles/Hr.	$\%H_2S^{(1)}$	$\%SO_2^{(2)}$	$H_2S/SO_2^{(3)}$	Temp., °F
5/28	4:24 PM	4.8	1570	0.38	0.20	1.90	212
5/28	4:50 PM	5.3	1570	0.38	0.20	1.90	248
5/29	12:00 M	8.8	1350	0.44	0.24	1.90	260
5/29	12:00 M	8.8	1350	0.44	0.24	1.90	260
5/29	7:30 PM	5.0	1560	0.39	0.20	1.95	221
5/29	10:30 PM	8.0	1600	0.37	0.20	1.85	221
5/30	0:30 AM	0.0	1630	0.37	0.19	1.95	212
5/30	3:20 AM	2.5	1600	0.37	0.20	1.85	212

Date	Time	Product Gas Composition, Mole %							Conversion, Mole %	
		N_2	O_2	CO	CO_2	H_2S	H_2O	SO_2	H_2S	SO_2
5/28	4:24 PM	77.4	2.0	-	15.0	0.12	5.4	0.08	68	60
5/28	4:50 PM	79.0	7.5	-	11.6	0.11	1.8	0.06	71	70
5/29	12:00 M	79.7	15.8	-	3.2	0.085	1.0	0.055	81	77
5/29	12:00 M	80.7	14.3	-	3.8	0.13	1.1	0.05	70	79
5/29	7:30 PM	-	-	-	-	0.036	-	0.21	91	-
5/29	10:30 PM	-	-	-	-	0.155	-	0.31	58	-
5/30	0:30 AM	-	-	-	-	0.055	-	0.20	85	-
5/30	3:20 AM	-	-	-	-	0.108	-	0.27	71	-

(1) Based on typical samples from H_2S generator
(2) Calculated from coal feed rate and sulfur composition
(3) See notes: 1, 2

TABLE IV-12

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst: -3/8" + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume
Space Velocity: 2050-2820 std. vol./vol./hr.
Flue Gas: Combustion of pulverized coal
Source of H_2S: Gas Bottles
Source of SO_2: Sulfur In Coal

			Flue Gas					
Date	Time	Hours on Stream[1]	Total GMFH[2]	V/V/Hr.	% H_2S	% SO_2	H_2S/SO_2	Temp.,°F
6/3	5:15 PM	4.8	1263	2150	0.38	0.19	2.0	212
6/3	8:30 PM	8.0	1263	2150	0.37	0.10	3.7	239
6/4	1:40 AM	3.2	1661	2820	0.28	0.14	2.0	221
6/4	4:30 AM	6.0	1661	2820	0.29	0.14	2.0	230
6/4	6:30 AM	8.0	1208	2050	0.40	0.46	0.9	230

		Product Gas Composition, Mole %						Conversion, Mole %	
Date	Time	N_2	O_2	CO_2	H_2S	H_2O	SO_2	H_2S	SO_2
6/3	5:15 PM	75.6	5.3	16.5	0.42	2.5	0.09	-	53
6/3	8:30 PM	78.2	6.8	12.0	0.36	2.7	0.08	3	20
6/4	1:40 AM	78.2	9.0	10.5	0.00	2.2	0.10	100	29
6/4	4:30 AM	78.2	9.4	10.0	0.35	2.0	0.07	-	50
6/4	6:30 AM	77.7	7.7	12.0	0.42	2.3	0.08	-	83

(1) After sulfur stripping and catalyst regeneration (2) Gram - moles per hour

TABLE IV-13
PILOT PLANT OPERATING DATA
SO_2 REDUCTION

Catalyst: -3/8" + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume
Space Velocity: 1140-1620 std. vol./vol./hr.
Flue Gas: Combustion of pulverized coal
Source of H_2S: Gas Bottles
Source of SO_2: Sulfur In Coal

Date	Time	Hours on Stream(1)	Flue Gas					
			Total GMPH(2)	V/V/Hr.	% H_2S	% SO_2	H_2S/SO_2	Temp., °F
6/5	4:20 AM	2.3	869	1480	0.54	0.56	1.0	275
6/7	2:00 AM	7.0	667	1140	0.72	0.77	0.9	248
6/10	12:25 PM	0.2	800	1350	0.64	0.56	1.1	257
6/10	2:45 PM	2.5	842	1430	0.59	0.27	2.1	221
6/11	6:10 PM	6.7	956	1620	0.47	0.54	0.9	203
6/11	10:20 PM	8.7	934	1590	0.48	0.56	0.9	203

Date	Time	Product Gas Composition, Mole %						Conversion, Mole %	
		N_2	O_2	CO_2	H_2S	H_2O	SO_2	H_2S	SO_2
6/5	4:20 AM	76.5	1.8	17.5	0.26	4.0	0.09	52	84
6/7	2:00 AM	79.9	1.1	15.5	0.93	2.5	0.01	-	99
6/10	12:25 PM	76.7	3.4	15.6	-	4.3	<0.01	-	>98
6/10	2:45 PM	78.7	18.4	2.4	0.04	0.5	0.03	93	89
6/11	6:10 PM	82.3	8.6	6.8	0.10	2.0	0.21	79	61
6/11	10:20 PM	81.7	5.4	10.6	0.13	2.0	0.21	73	62

(1) After sulfur stripping and catalyst regeneration (2) Gram - moles per hour

TABLE IV-14

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst: -3/8" + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume

Space Velocity: 1080-2110 std. vol./vol./hr.

Flue Gas: Combustion of natural gas

Source of H_2S: Gas Bottles

Source of SO_2: Gas Bottles

			Flue Gas					
Date	Time	Hours on Stream[1]	Total GMPH[2]	V/V/Hr.	% H_2S	% SO_2	H_2S/SO_2	Temp., °F
6/24	12:30 PM	0.0	896	1520	0.68	0.26	2.6	-
6/25	8:55 AM	9.0	638	1080	0.96	0.36	2.6	176
6/27	6:45 AM	0.3	1243	2110	0.49	0.19	2.6	212
6/27	3:30 PM	9.0	1017	1725	0.62	0.23	2.7	221
6/27	8:40 PM	2.2	901	1530	0.72	0.27	2.7	212
6/28	3:55 AM	6.4	864	1470	0.69	0.27	2.6	203

		Product Gas Composition, Mole %						Conversion, Mole %	
Date	Time	N_2	O_2	CO_2	H_2S	H_2O	SO_2	H_2S	SO_2
6/24	12:30 PM	76.2	1.6	8.2	0.04	10.8	0.05	94	81
6/25	8:55 AM	77.5	1.0	9.8	0.11	11.6	0.02	89	94
6/27	6:45 AM	78.6	1.5	16.0	0.0	3.5	0.09	100	52
6/27	3:30 PM	65.6	3.1	8.8	0.14	22.3	0.08	78	61
6/27	8:40 PM	86.1	1.6	10.8	0.10	1.1	0.03	86	89
6/28	3:55 AM	74.4	0.8	8.9	0.28	13.3	0.01	60	96

(1) After sulfur stripping and catalyst regeneration (2) Gram - moles per hour

TABLE IV-15

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst: -3/8" + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume
Space Velocity: 1875 std. vol./vol./hr.
Flue Gas: Combustion of natural gas
Source of H_2S: Gas bottles
Source of SO_2: Gas bottles

			Flue Gas					
Date	Time	Hours on Stream[1]	Total GMPH[2]	V/V/Hr.	%H_2S	%SO_2	H_2S/SO_2	Temp., °F
7/1	4:50 PM	0.3	1102	1875	0.54	0.23	2.4	212
7/1	7:12 PM	2.7	1102	1875	0.54	0.23	2.4	212
7/1	9:15 PM	4.8	1102	1875	0.54	0.23	2.4	212
7/2	0:15 AM	7.8	1102	1875	0.54	0.23	2.4	212

		Product Gas Composition, Mole %							Conversion, Mole %	
Date	Time	N_2	O_2	CO_2	H_2S	H_2O	SO_2	CH_4	H_2S	SO_2
7/1	4:50 PM	81.2	1.3	9.2	0.06	4.0	0.02	4.4	89	91
7/1	7:12 PM	75.3	1.5	7.9	0.04	11.0	0.04	4.3	93	83
7/1	9:15 PM	74.4	1.5	7.8	0.04	12.0	0.04	4.3	93	83
7/2	0:15 AM	74.5	1.6	8.7	0.25	11.3	0.09	4.3	54	61

(1) After sulfur stripping and catalyst regeneration

(2) Gram-moles per hour

TABLE IV-16
PILOT PLANT OPERATING DATA
SO_2 REDUCTION

Catalyst: -3/8" + 1/4" Alcoa F-1 Activated Alumina Granules; 0.49 ft.^{3} volume
Space Velocity: 1550 Std. vol./vol./hr.
Flue Gas: Combustion of natural gas
Source of H_2S: Gas bottles
Source of SO_2: Gas bottles

			Flue Gas					
Date	Time	Hours on Stream (1)	Total GMPH (2)	V/V/Hr.	%H_2S	%SO_2	H_2S/SO_2	Temp., °F
7/7	6:00 PM	0.0	914	1550	0.65	0.26	2.5	203
7/7	9:10 PM	3.2	914	1550	0.65	0.26	2.5	212
7/8	0:30 AM	6.5	914	1550	0.65	0.26	2.5	212
7/8	3:15 AM	9.3	914	1550	0.65	0.26	2.5	212
7/8	10:43 AM	4.7	914	1550	0.65	0.26	2.5	230

		Product Gas Composition, Mole %							Conversion, Mole %	
Date	Time	N_2	O_2	CO_2	H_2S	H_2O	SO_2	CH_4	H_2S	SO_2
7/7	6:00 PM	76.4	2.3	9.0	0.20	9.0	0.02	3.2	69	92
7/7	9:10 PM	76.8	1.4	9.1	0.03	9.5	0.05	3.5	95	81
7/8	0:30 AM	76.3	1.2	8.8	0.12	10.0	0.12	3.5	82	54
7/8	3:15 AM	76.7	1.2	8.9	0.20	9.3	0.18	3.5	69	31
7/8	10:43 AM	78.4	1.5	7.2	0.02	9.8	<0.02	3.1	97	94

TABLE IV-17

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Catalyst: 1/8" x 1/4" Linde 13X Molecular Sieve Extrusions

Space Velocity: 1500 Std. vol./vol./hr.

Temperature: 212°F

Flue Gas: Combustion of natural gas (spot samples indicated about 5% residual methane in flue gas.)

Source of H_2S, SO_2, NO_x: Gas bottles

Run No.	Feed			Conversion			Comments
	Hrs. on Stream	H_2S/SO_2	% SO_2	Hrs. on Stream	% H_2S Conv.	% SO_2 Conv.	
MS1-1	1:40	0.80	0.47	3:00	85	>97.4	Initial charge.
	4:30	1.47	0.32	8:30	69	94.8	No NO_x.
	8:10	1.73	0.40				
	Av.	1.33	0.40	Av.	77	>96.1	
MS1-2	0.55	N.A.	-	1:40	76	N.A.	No NO_x.
	2.25	1.74	0.28	3:25	66	97.3	
	4:45	2.33	0.19	5:50	89.3	75	
	7:10	1.68	0.27	8:10	52	48	
	10:25	2.08	0.25				
	Av.	1.96	0.25	Av.	71	73	
MS1-3	0:30	0.84	0.25	1:35	60	74	Low H_2S/SO_2 ratio during
	2:45	0.89	0.27	4:15	45	73	1st half of run.
	5:25	1.78	0.27	6:45	65	77	500 ppm NO_x added.
	8:10	1.74	0.32	9:30	52	68	
	Av.	1.31	0.30	Av.	55.5	73	
MS1-4	1:30	1.77	0.25	3:15	50	70	500 ppm NO_x added.
	4:14	1.97	0.31				
	Av.	1.87	0.28	Av.	50	70	
MS1-5	0:50	1.84	0.28	2:05	76	86	No NO_x.
	4:18	1.94	0.28	5:30	55	62	
	6:45	1.66	0.30	8:15	49	40	
	Av.	1.81	0.29	Av.	60	63	

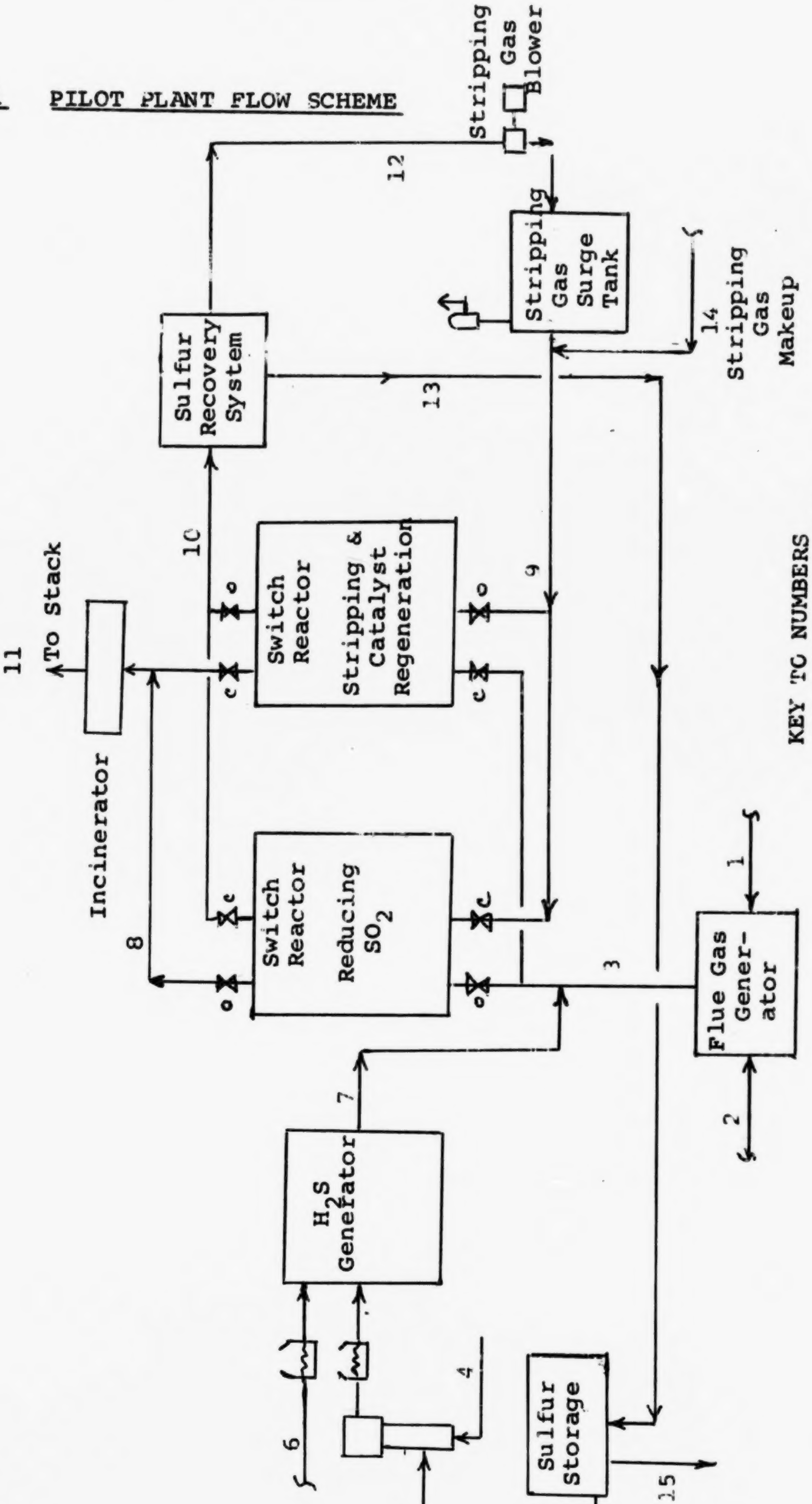
TABLE IV-17 (cont.)

PILOT PLANT OPERATING DATA

SO_2 REDUCTION

Run No.	Feed Hrs. on Stream	H_2S/SO_2	$\%SO_2$	Conversion Hrs. on Stream	$\% H_2S$ Conv.	$\% SO_2$ Conv.	Comments
MS1-6	2:50	2.01	0.22	1:30	76	75	No NO_x.
	8:00	2.35	0.26	6:20	68	82	
	Av.	2.18	0.24	9:10	67	74	
				Av.	70	77	
MS2-1	2:30	2.97	0.19	1:10	84	100.	New charge, 500 ppm NO_x added for 1st 7 hrs. on stream; no NO_x for remainder of run
	6:30	3.13	0.19	2:41	70	90.1	
	6:30	2.74	0.24	7:15	57	79	
	7:05	2.65	0.26	7:30	65	90.3	
				8:20	58	80	
	Av.	2.87	0.22	Av.	67	88	

FIGURE IV-1 PILOT PLANT FLOW SCHEME

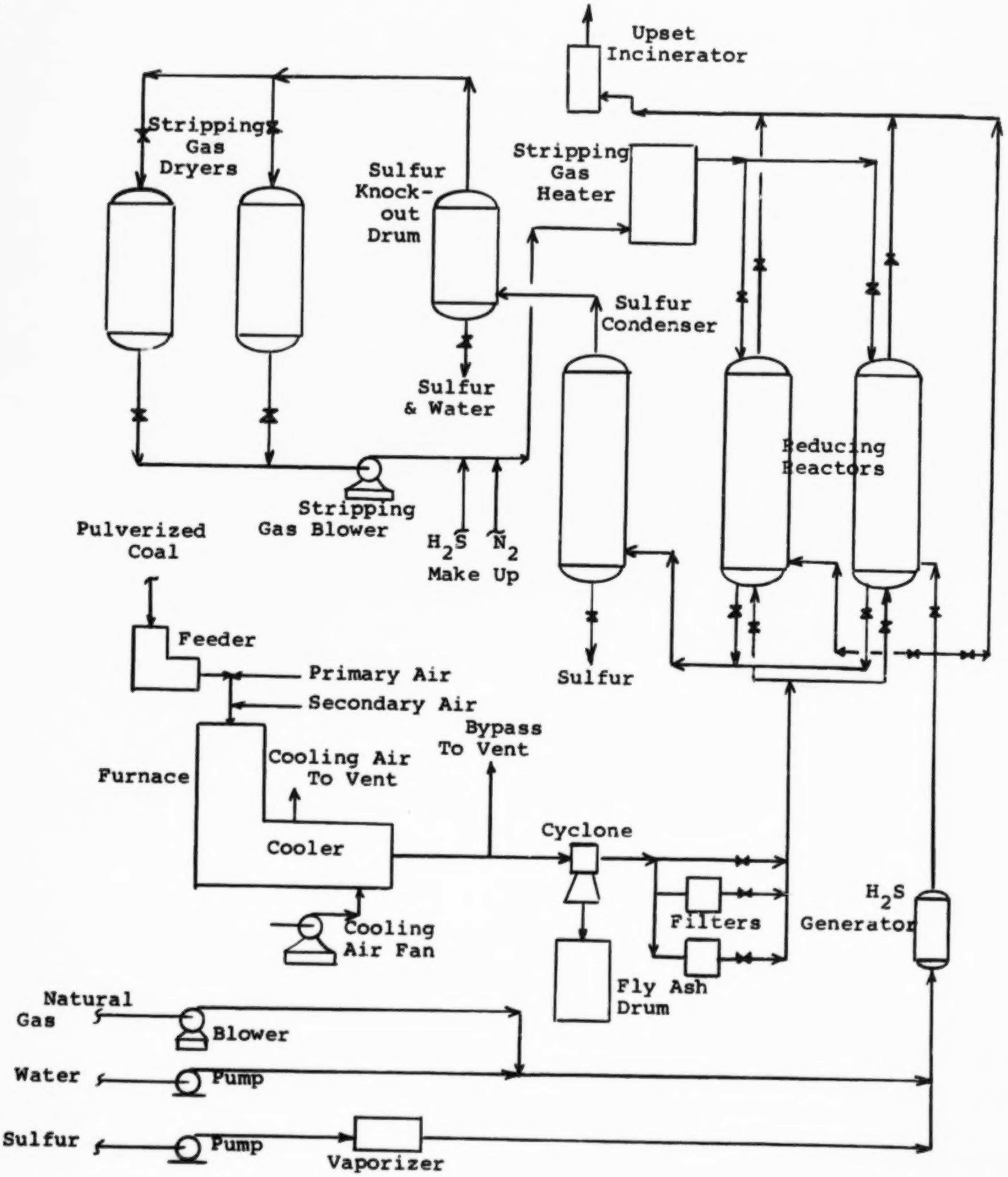

Stripping Gas Blower
12
Stripping Gas Surge Tank
14
Stripping Gas Makeup
Sulfur Recovery System
13
10
Switch Reactor
Stripping & Catalyst Regeneration
9
To Stack
11
Incinerator
Switch Reactor
Reducing SO_2
8
3
1
Flue Gas Generator
2
7
H_2S Generator
4
6
5
Sulfur Storage
15
o
c

KEY TO NUMBERS ON FOLLOWING PAGE

KEY TO FIGURE IV-1 PILOT PLANT FLOW SCHEME

Stream Number	Identification
1	Pulverized Coal - 8.5 pounds/hour
2	Combustion Air - 22.5 SCFM
3	Flue Gas - 23.3 SCFM (0.2% SO_2)
4	Natural Gas - 0.025 SCFM
5	Sulfur Recycle - .0189 SCFM (as S_5)
6	Water For H_2S Generation - .063 SCFM
7	Reducing Stream - 0.135 SCFM (70% H_2S)
8	"SO_2-Free Flue Gas" - 23.3 SCFM (0.01% SO_2)
9	Stripping Gas - 10 SCFM ($<$5% H_2S)
10	Stripping Gas Carrying Sulfur - 10 SCFM
11	Incinerated Flue Gas - 23.3 SCFM
12	Sulfur-Free Stripping Gas - 10 SCFM
13	Sulfur Recovered
14	Stripping Gas Makeup
15	Sulfur Product - $>$5 pounds/day

FIGURE IV-2
PILOT PLANT FLOWSHEET

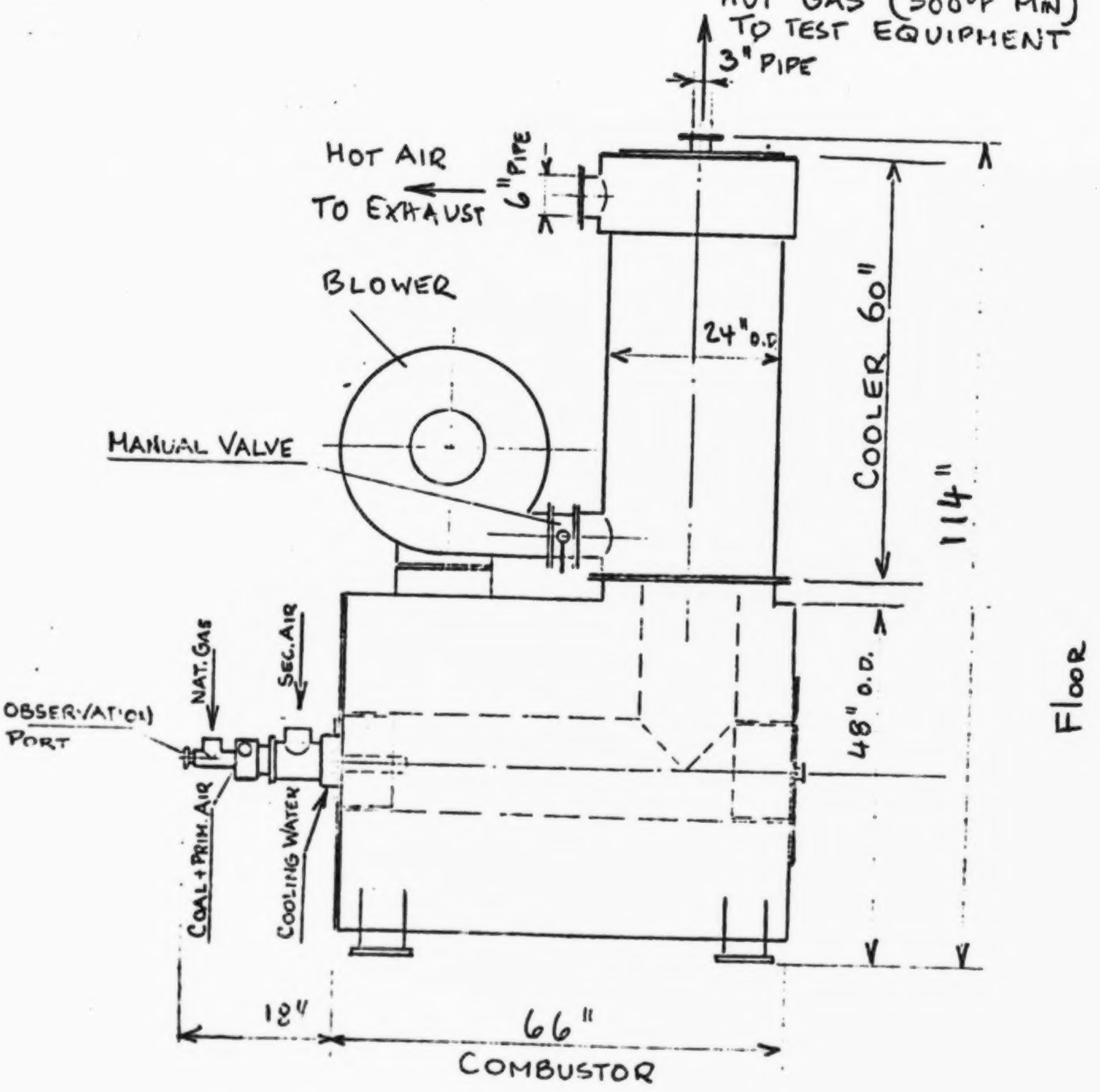

Upset Incinerator
Stripping Gas Dryers
Sulfur Knock-out Drum
Stripping Gas Heater
Sulfur Condenser
Sulfur & Water
Reducing Reactors
Stripping Gas Blower
Pulverized Coal
H_2S
N_2
Make Up
Feeder
Primary Air
Secondary Air
Sulfur
Bypass To Vent
Furnace
Cooling Air To Vent
Cooler
Cyclone
Filters
H_2S Generator
Cooling Air Fan
Fly Ash Drum
Natural Gas
Blower
Water
Pump
Sulfur
Pump
Vaporizer

GENERAL DIVISION, IONICS, INCORPORATED
P. O. BOX 99, BRIDGEVILLE, PA. 15017 (412) 343-1040

PROJECT Princeton Chem. Res, Inc.
SUBJECT Coal Combustor and Cooler

NUMBER 3660
SHEET NUMBER ____ OF ____
DATE 8-15-68
COMPUTED BY ____
CHECKED BY ____

FIGURE IV-3
PILOT PLANT COMBUSTOR-COOLER SCHEMATIC


HOT GAS (300°F MIN) TO TEST EQUIPMENT
3" PIPE
HOT AIR TO EXHAUST
6" PIPE
BLOWER
24" O.D.
COOLER 60"
MANUAL VALVE
114"
FLOOR
NAT. GAS
SEC. AIR
OBSERVATION PORT
48" O.D.
COAL + PRIM. AIR
COOLING WATER
18"
66"
COMBUSTOR

NERAL DIVISION, IONICS, INCORPORATED
P. O. BOX 99, BRIDGEVILLE, PA. 15017 (412) 343-1040

PROJECT Princeton Chem. Research
SUBJECT Piping & Wiring Diagram

NUMBER 3660
SHEET NUMBER ____ OF ____
DATE 12-3-68
COMPUTED BY ____
CHECKED BY Rev 1-4-69

ALL PIPING & WIRING SHOWN BY IONICS INC.

FIGURE IV-4

PILOT PLANT COMBUSTOR COOLER

ORIGINAL PIPING AND WIRING SCHEMATIC

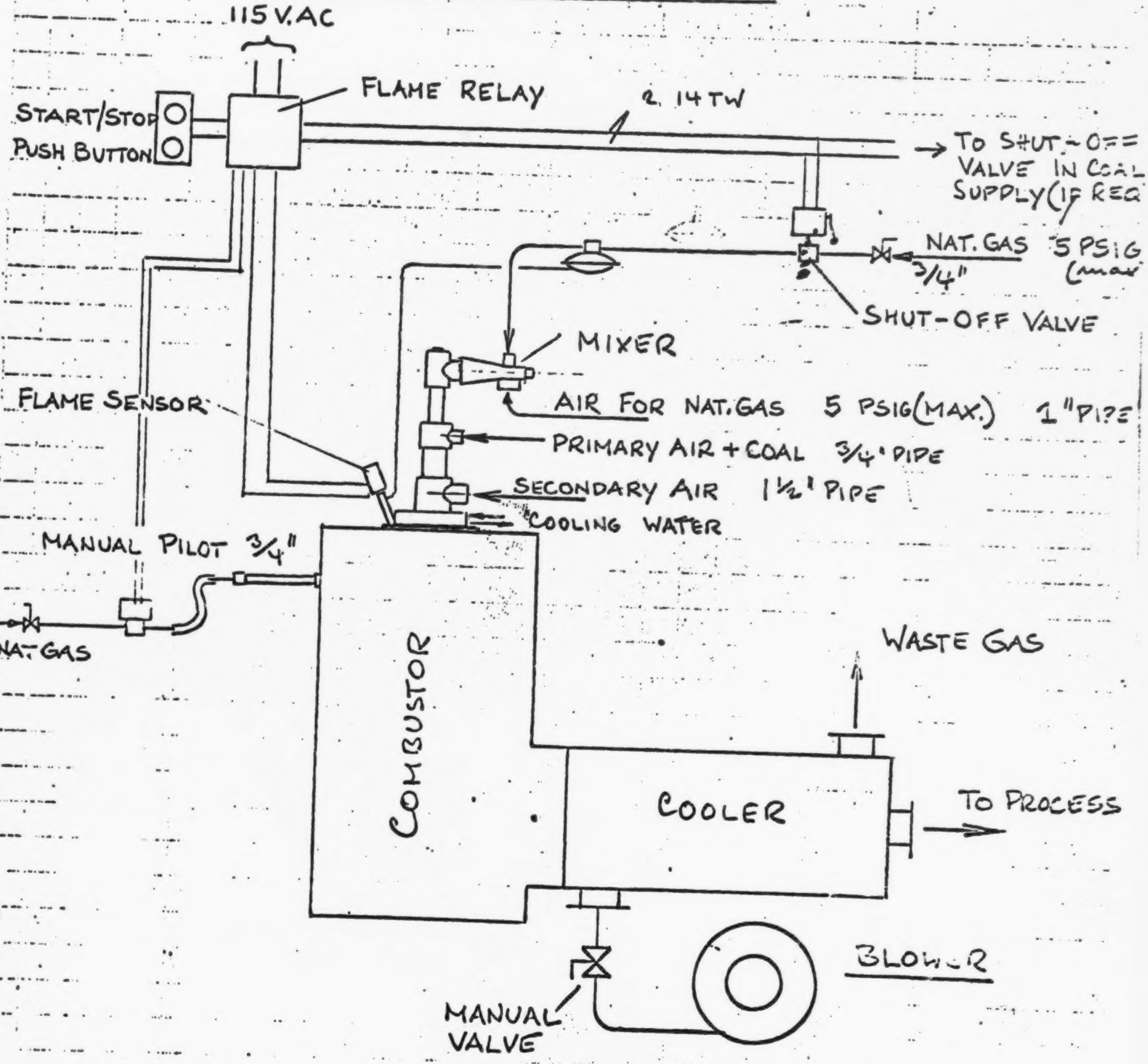

115 V.AC
FLAME RELAY
2. 14TW
START/STOP PUSH BUTTON
→ TO SHUT-OFF VALVE IN COAL SUPPLY (IF REQ
NAT. GAS 3/4"
5 PSIG (MAX
SHUT-OFF VALVE
MIXER
AIR FOR NAT. GAS 5 PSIG (MAX.) 1" PIPE
FLAME SENSOR
PRIMARY AIR + COAL 3/4" PIPE
SECONDARY AIR 1½" PIPE
COOLING WATER
MANUAL PILOT 3/4"
NAT. GAS
COMBUSTOR
WASTE GAS
COOLER
TO PROCESS
BLOWER
MANUAL VALVE

FIGURE IV-5 COMBUSTOR - COOLER GENERAL ASSEMBLY

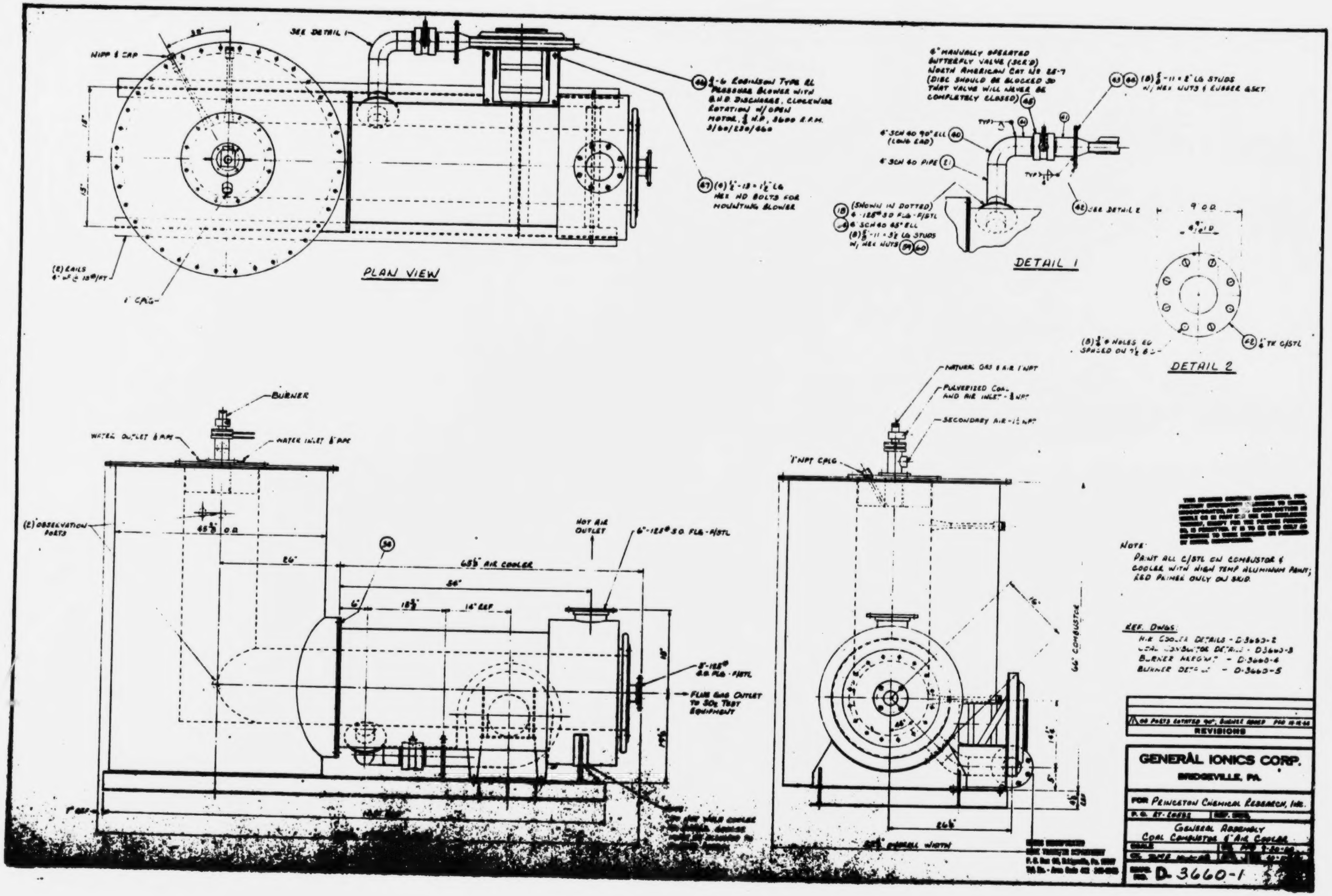
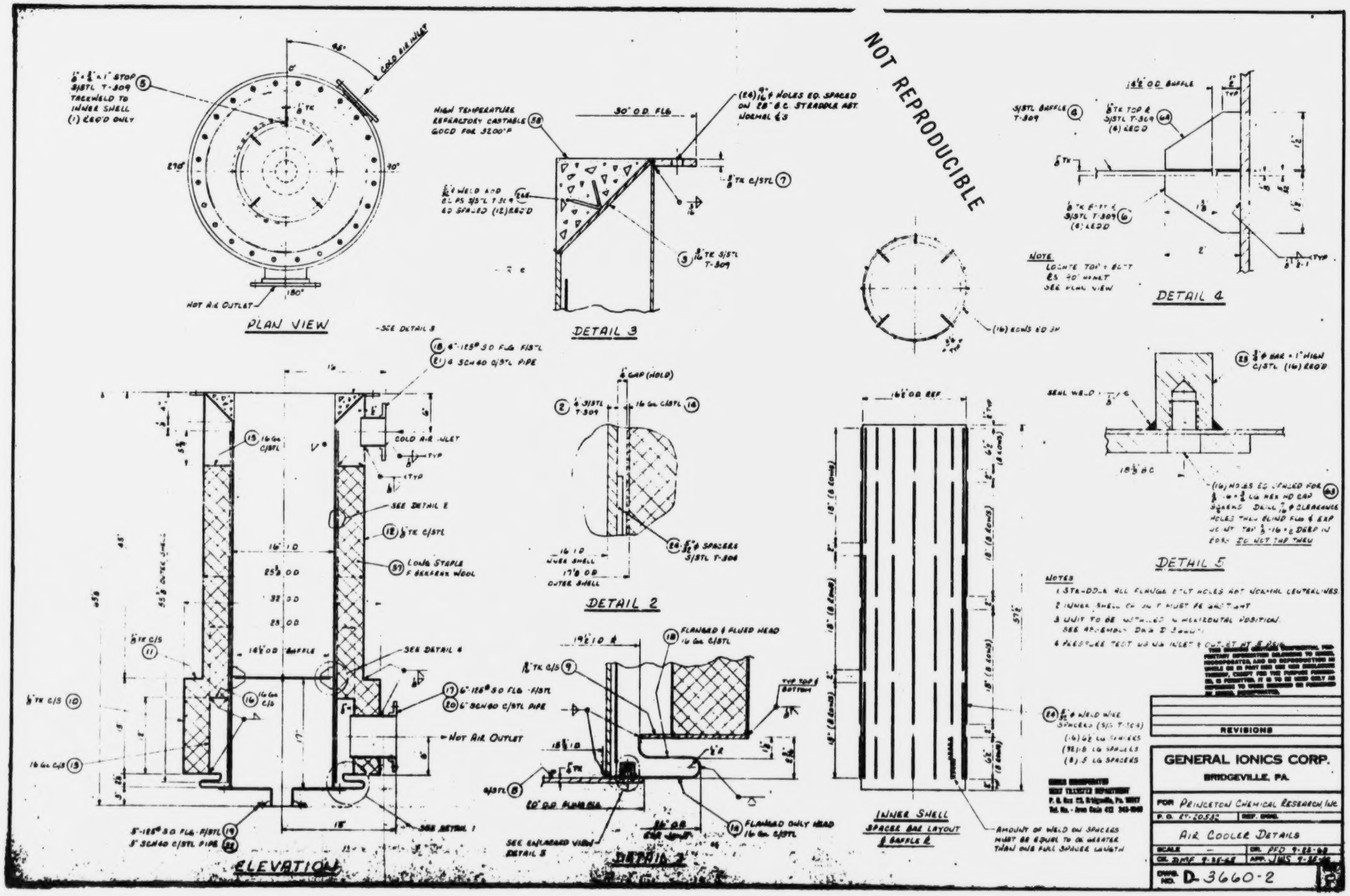

PLAN VIEW
SEE DETAIL 1
NIPP & CAP
38°
18"
18"
(2) RAILS 4" ⊏ @ 13#/FT
1" CPLG
(66) 8-6 ROBINSON TYPE RL PRESSURE BLOWER WITH B.H.D. DISCHARGE, CLOCKWISE ROTATION W/ OPEN MOTOR, ¾ H.P., 3600 R.P.M. 3/60/230/460
(67) (4) ½"-13 × 1½" LG HEX HD BOLTS FOR MOUNTING BLOWER
6" MANUALLY OPERATED BUTTERFLY VALVE (SCR'D) NORTH AMERICAN CAT NO 28-7 (DISC SHOULD BE BLOCKED SO THAT VALVE WILL NEVER BE COMPLETELY CLOSED) (45)
(43) (44) (8) ⅝"-11 × 2" LG STUDS W/ HEX NUTS & RUBBER GSKT
6" SCH 40 90° ELL (LONG RAD) (40)
6" SCH 40 PIPE (21)
TYP
(41)
(18) (SHOWN IN DOTTED) 6"-125# SO FLG-F/STL
6" SCH 40 45° ELL
(8) ⅝"-11 × 3½" LG STUDS W/ HEX NUTS (59) (60)
(42) SEE DETAIL 2
DETAIL 1
9" O.D.
6⅝" I.D.
(8) ¾" ⌀ HOLES EQ SPACED ON 7½" B.C.
(42) ¼" TK C/STL
DETAIL 2
BURNER
WATER OUTLET ½" NPT
WATER INLET ½" NPT
(2) OBSERVATION PORTS
45⅝" O.D.
26"
(34)
65½" AIR COOLER
56"
6"
18⅝"
14" REF
HOT AIR OUTLET
6"-125# S.O. FLG-F/STL
8"-125# S.O. FLG-F/STL
FLUE GAS OUTLET TO SO2 TEST EQUIPMENT
18"
14½"
1" REF
NATURAL GAS & AIR 1" NPT
PULVERIZED COAL AND AIR INLET - ¾" NPT
SECONDARY AIR - 1½" NPT
1" NPT CPLG
16"
66" COMBUSTOR
14½"
5"
4½"
26½"
80½" OVERALL WIDTH
[redacted]
NOTE:
PAINT ALL C/STL ON COMBUSTOR & COOLER WITH HIGH TEMP ALUMINUM PAINT; RED PRIMER ONLY ON SKID.
REF. DWGS:
AIR COOLER DETAILS - D-3660-2
COAL COMBUSTOR DETAILS - D-3660-3
BURNER ARRG'MT - D-3660-4
BURNER DETAIL - D-3660-5
REVISIONS
GENERAL IONICS CORP.
BRIDGEVILLE, PA.
FOR PRINCETON CHEMICAL RESEARCH, INC.
GENERAL ASSEMBLY
COAL COMBUSTOR & AIR COOLER
D-3660-1

FIGURE IV-6 FLUE GAS COOLER DETAILS


NOT REPRODUCIBLE
PLAN VIEW
COLD AIR INLET
HOT AIR OUTLET
45°
0°
90°
180°
270°
⑤ 1/8" × 3/8" × 1" STOP S/STL T-309 TACKWELD TO INNER SHELL (1) REQ'D ONLY
DETAIL 3
HIGH TEMPERATURE REFRACTORY CASTABLE GOOD FOR 3200°F
30" O.D. FLG
(24) 9/16" ⌀ HOLES EQ. SPACED ON 28" B.C. STRADDLE NORMAL ℄S
1/8" TK C/STL ⑦
3/16" TK S/STL T-309 ③
DETAIL 4
18 1/8" O.D. BAFFLE
S/STL BAFFLE ④ T-309
NOTE LOCATE TOP & BOTT ℄S 90° APART SEE PLAN VIEW
(16) ROWS EQ SP
ELEVATION
⑱ 4"-125# S.O. FLG S/STL
㉑ 4 SCH 40 C/STL PIPE
COLD AIR INLET
HOT AIR OUTLET
SEE DETAIL 2
SEE DETAIL 4
SEE DETAIL 1
⑫ 1/8" TK C/STL
⑬ 16 Ga C/STL
㊲ LONG STAPLE FIBERFRAX WOOL
16" I.D.
25 3/4" O.D.
32 O.D.
25 O.D.
18 1/8" O.D. BAFFLE
⑰ 6"-125# S.O. FLG S/STL
⑳ 6" SCH 40 C/STL PIPE
⑲ 5"-125# S.O. FLG S/STL
5" SCH 40 C/STL PIPE
1/8" TK C/S ⑩
1/8" TK C/S ⑪
16 Ga C/S ⑬
DETAIL 2
1/8" GAP (HOLD)
② 1/4" S/STL T-309
16 Ga C/STL ⑭
16 I.D. INNER SHELL
17 1/8" O.D. OUTER SHELL
㉔ 5/32" ⌀ SPACERS S/STL T-304
FLANGED & FLUED HEAD 16 Ga C/STL
FLANGED ONLY HEAD 16 Ga C/STL
1/8" TK C/S ⑨
20" O.D. PLUMB
SEE ENLARGED VIEW DETAIL 5
INNER SHELL SPACER BAR LAYOUT & BAFFLE ℄
16 1/8" O.D. REF.
AMOUNT OF WELD ON SPACERS MUST BE EQUAL TO OR GREATER THAN ONE FULL SPACER LENGTH
DETAIL 5
SEAL WELD
18 3/8" B.C.
3/8" ⌀ BAR × 1" HIGH C/STL (16) REQ'D
(16) HOLES EQ. SPACED FOR 3/8" - 16 × 3/4" LG HEX HD CAP SCREWS. DRILL 7/16" ⌀ CLEARANCE HOLES THRU BLIND FLG & EXP JOINT. TAP 3/8" - 16 × 1/2" DEEP IN EXP. DO NOT TAP THRU
㉔ 5/32" ⌀ WELD WIRE SPACERS (S/S T-304)
(16) 6 1/2" LG SPACERS
(32) 18 LG SPACERS
(8) 5 LG SPACERS

NOTES
1 STRADDLE ALL FLANGE BOLT HOLES ABT NORMAL CENTERLINES.
2 INNER SHELL OR JOINT MUST BE GAS TIGHT
3 UNIT TO BE INSTALLED IN HORIZONTAL POSITION. SEE ASSEMBLY DWG D-3660-1
4 PRESSURE TEST USING INLET & OUTLET AT 5 PSIG

REVISIONS

GENERAL IONICS CORP.
BRIDGEVILLE, PA.

FOR PRINCETON CHEMICAL RESEARCH, INC
P.O. 27-20582
REF. DWG.

AIR COOLER DETAILS

SCALE —
DR. PFD 9-25-68
CK. DMF 9-25-68
APP. JWS 9-25-68
DWG. NO. D-3660-2

FIGURE IV-7 COAL COMBUSTOR DETAILS

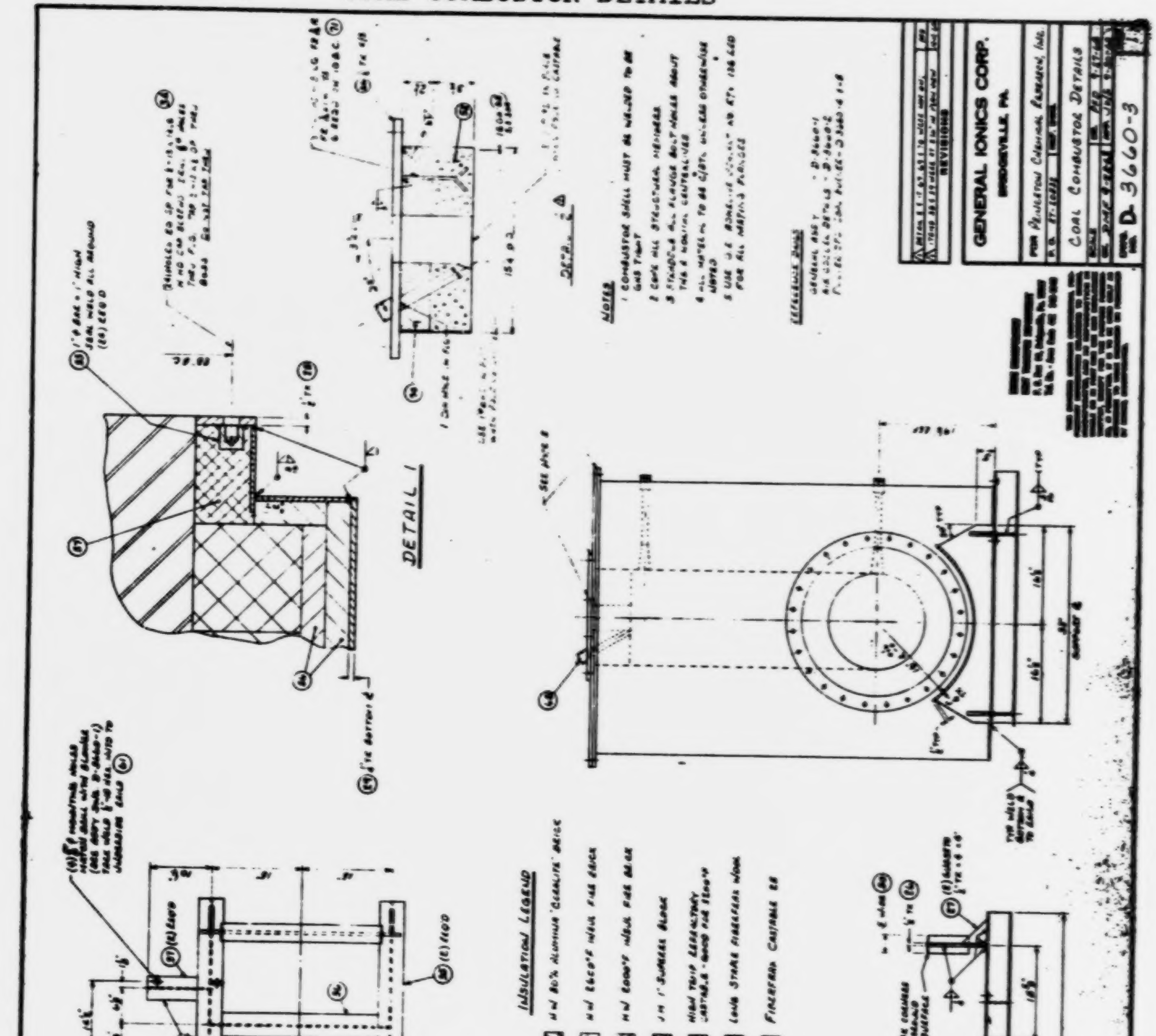

PLAN VIEW
DETAIL 1
INSULATION LEGEND
NOTES
GENERAL IONICS CORP.
BRIDGEVILLE, PA.
COAL COMBUSTOR DETAILS
D-3660-3

FIGURE IV-8 COAL BURNER GENERAL ASSEMBLY

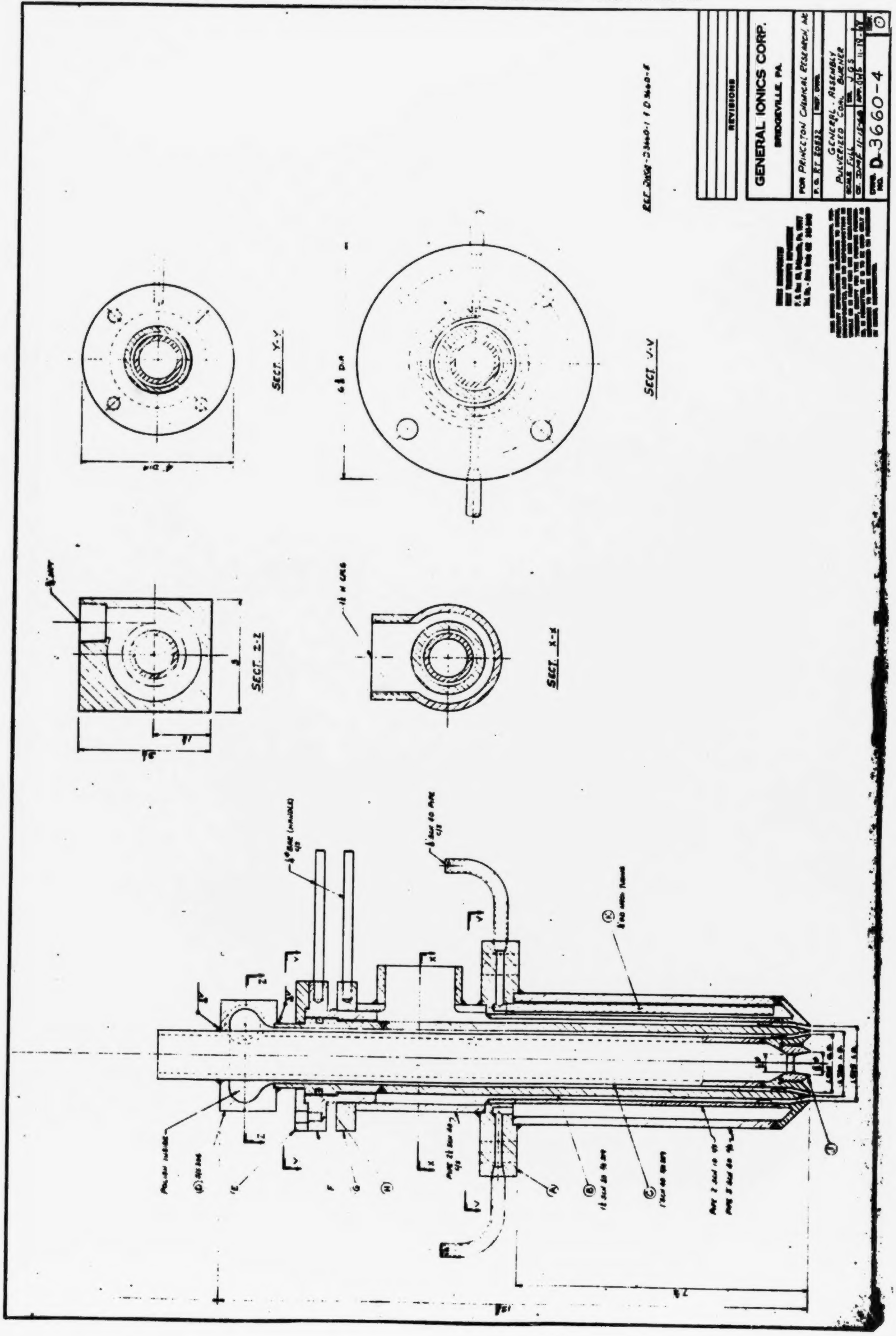

REVISIONS
GENERAL IONICS CORP.
BRIDGEVILLE, PA.
FOR PRINCETON CHEMICAL RESEARCH, INC
GENERAL ASSEMBLY
PULVERIZED COAL BURNER
SCALE FULL
D-3660-4
SECT. Y-Y
SECT. V-V
SECT. Z-Z
SECT. X-X

FIGURE IV-9 COAL BURNER DETAILS

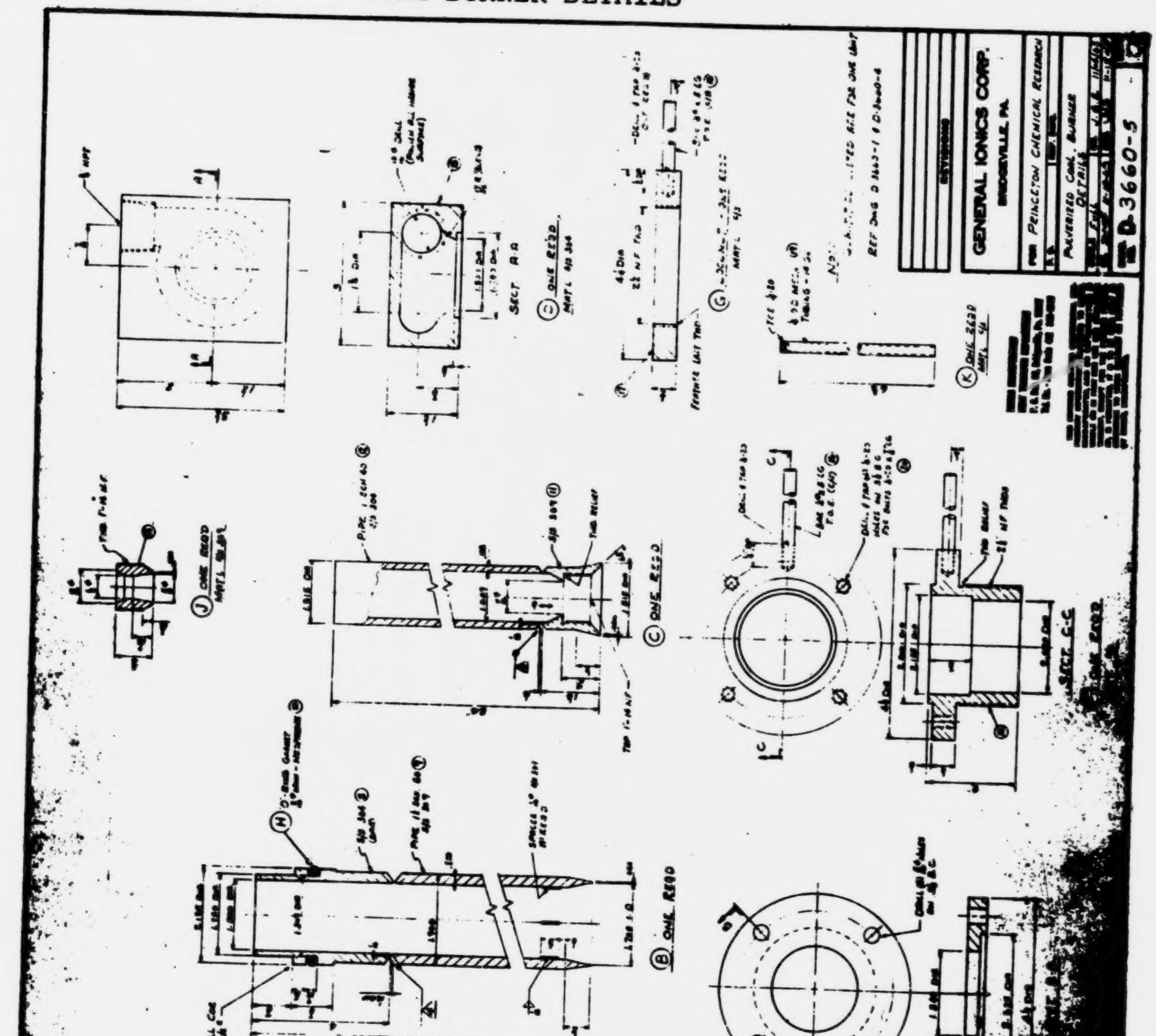

GENERAL IONICS CORP.
BRIDGEVILLE, PA.
FOR PRINCETON CHEMICAL RESEARCH
PULVERIZED COAL BURNER DETAILS
D-3660-5
B ONE REQD
C ONE REQD
J ONE REQD
K ONE REQD
SECT. C-C
NOT REPRODUCIBLE

FIGURE IV - 10
PILOT PLANT FLUE GAS GENERATION SECTION

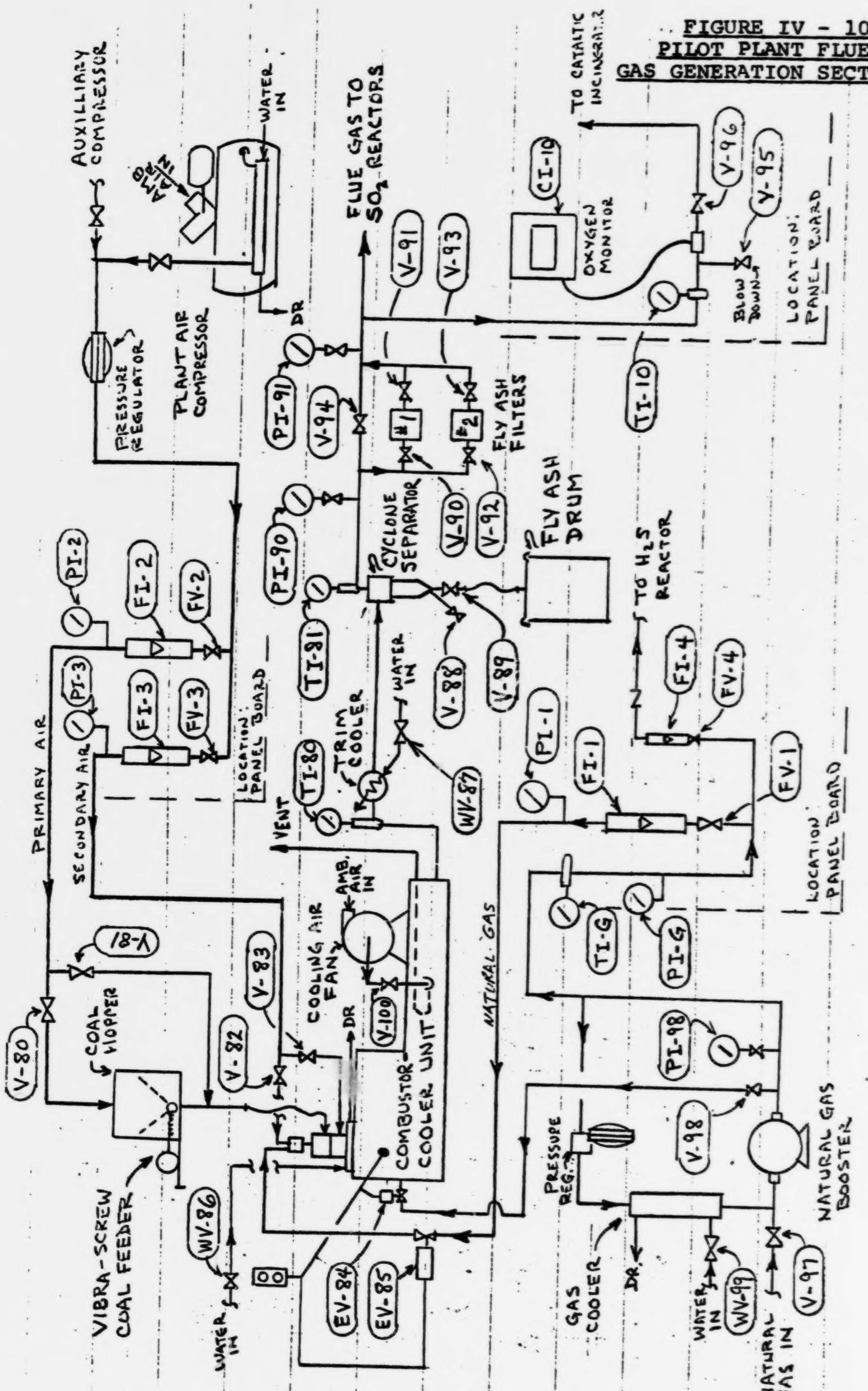
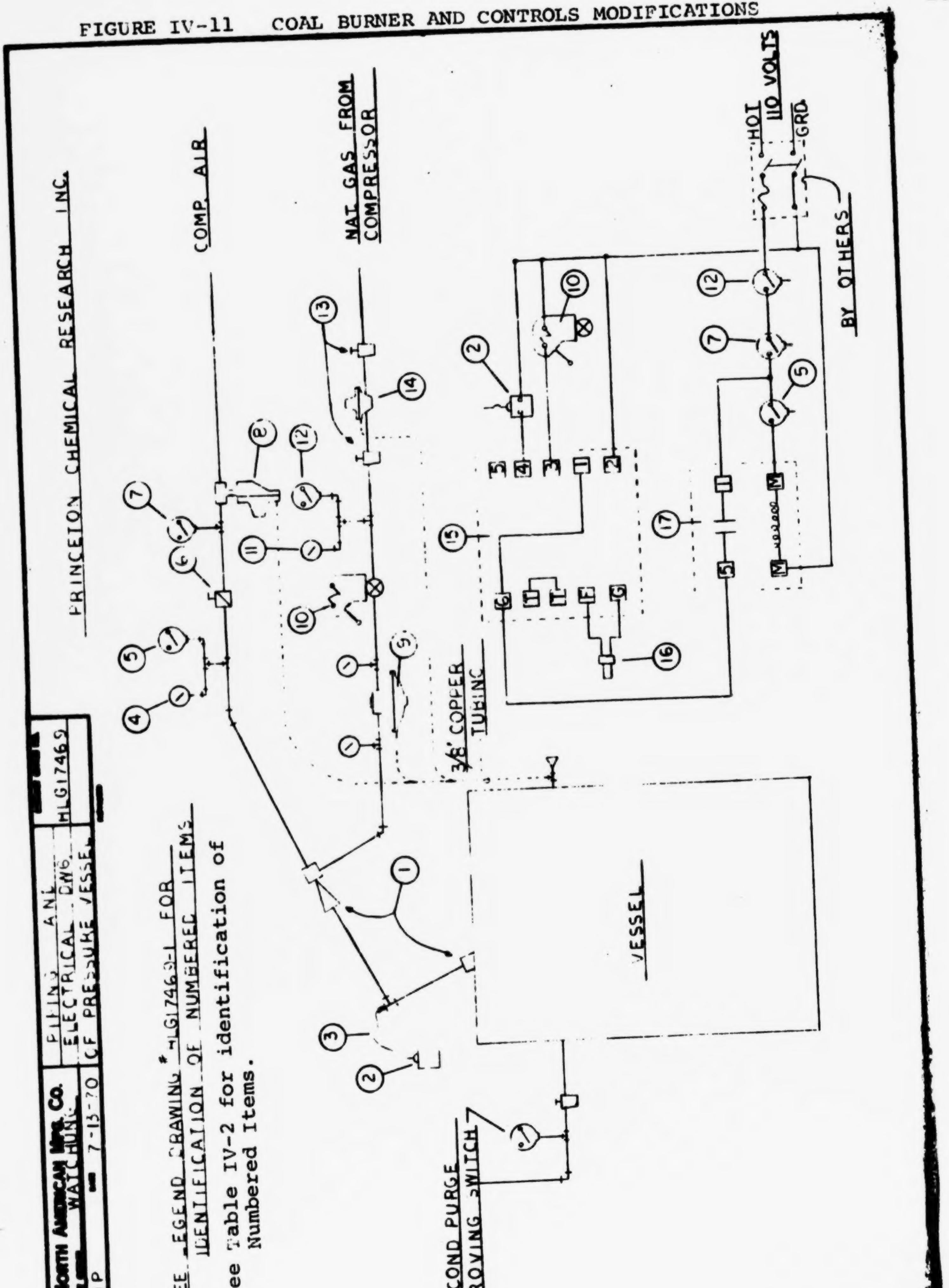

AUXILLIARY COMPRESSOR
AIR IN
WATER IN
DR
PLANT AIR COMPRESSOR
PRESSURE REGULATOR
PRIMARY AIR
SECONDARY AIR
PI-2
FI-2
FV-2
PI-3
FI-3
FV-3
LOCATION: PANEL BOARD
V-80
V-81
COAL HOPPER
V-82
V-83
VIBRA-SCREW COAL FEEDER
WATER IN
WV-86
COOLING AIR FAN
AMB. AIR IN
VENT
DR
V-100
COMBUSTOR COOLER UNIT
EV-84
EV-85
TI-80
TRIM COOLER
WATER IN
WV-87
TI-81
CYCLONE SEPARATOR
PI-90
V-88
V-89
FLY ASH DRUM
PI-91
V-94
#1
#2
FLY ASH FILTERS
V-90
V-92
V-91
V-93
FLUE GAS TO SO$_2$ REACTORS
TO CATALYTIC INCINERATOR
CI-10
OXYGEN MONITOR
V-96
V-95
BLOW DOWN
TI-10
LOCATION: PANEL BOARD
NATURAL GAS
PI-1
FI-1
FV-1
FI-4
FV-4
TO H$_2$S REACTOR
TI-G
PI-G
LOCATION PANEL BOARD
PI-98
V-98
PRESSURE REG.
GAS COOLER
DR.
WATER IN
WV-99
NATURAL GAS IN
V-97
NATURAL GAS BOOSTER

FIGURE IV-11   COAL BURNER AND CONTROLS MODIFICATIONS


THE NORTH AMERICAN MFG. CO.
WATCHUNG
7-13-70
JP
PIPING AND ELECTRICAL DWG.
CF PRESSURE VESSEL
HLG17469
PRINCETON CHEMICAL RESEARCH INC.
SEE LEGEND DRAWING #HLG17469-1 FOR IDENTIFICATION OF NUMBERED ITEMS
COMP. AIR
NAT GAS FROM COMPRESSOR
HOT
110 VOLTS
GRD
BY OTHERS
3/8" COPPER TUBING
VESSEL
SECOND PURGE PROVING SWITCH
1
2
3
4
5
6
7
8
10
11
12
13
14
15
16
17
M
M
5
11
G
L1
L
F
G
5
4
3
1
2

See Table IV-2 for identification of Numbered Items.

FIGURE IV-12 COAL FEEDER ENGINEERING DRAWING

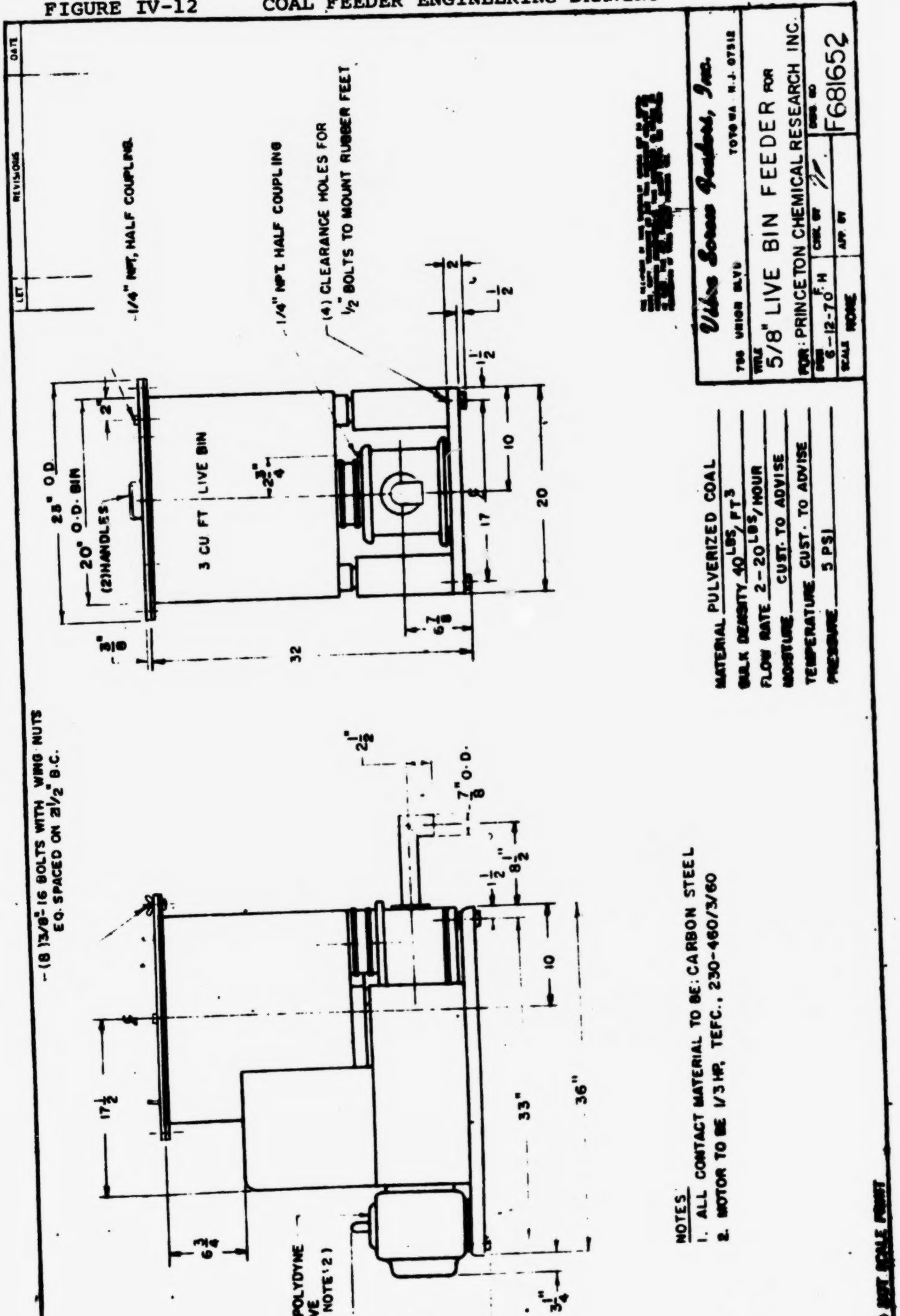
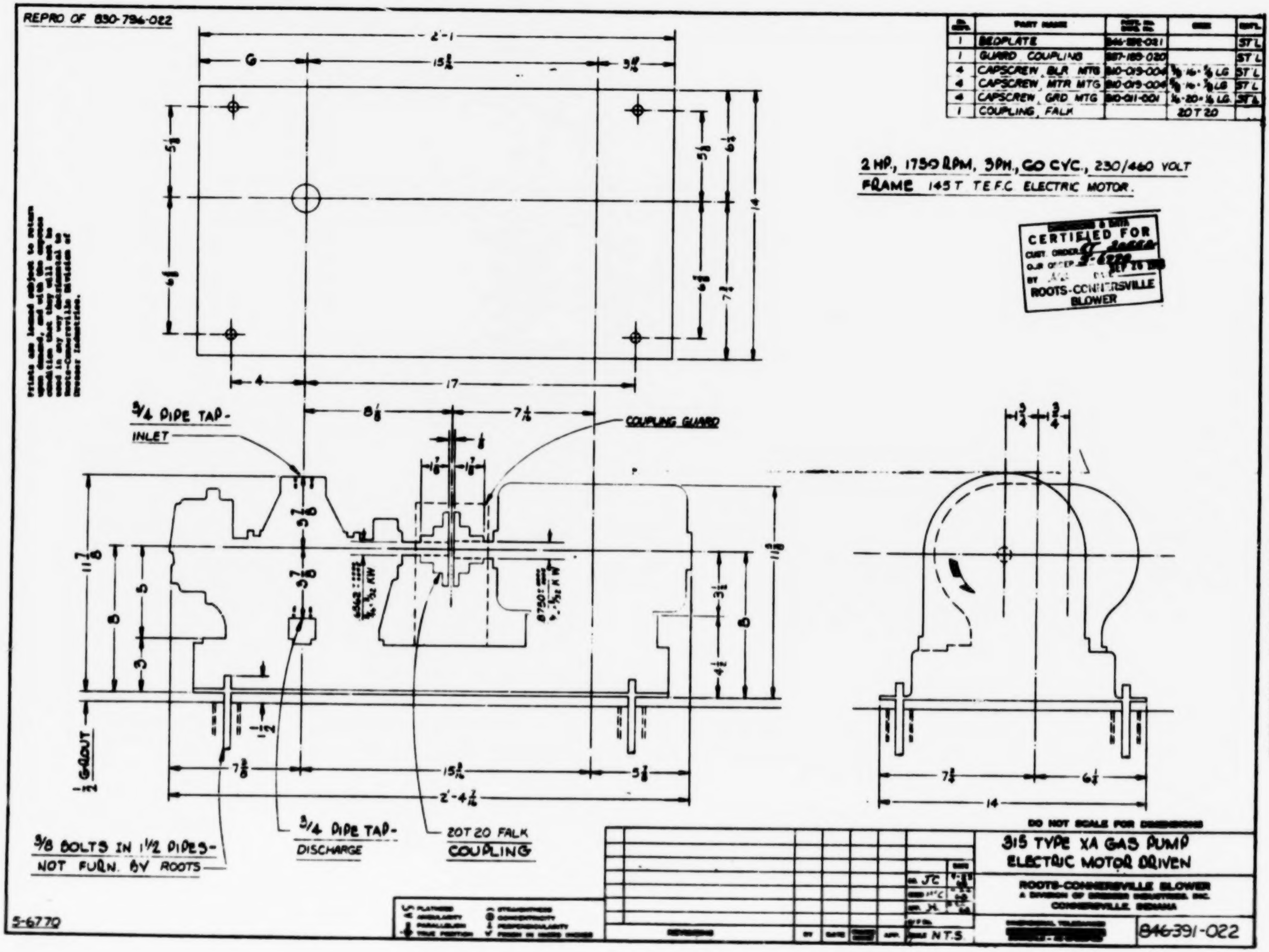

LET
REVISIONS
DATE
-1/4" NPT, HALF COUPLING
-1/4" NPT HALF COUPLING
(4) CLEARANCE HOLES FOR 1/2" BOLTS TO MOUNT RUBBER FEET
25" O.D.
20" O.D. BIN
(2) HANDLES
3 CU FT LIVE BIN
$2\frac{3}{4}$
2
$1\frac{1}{2}$
$\frac{1}{2}$
2
10
17
20
$6\frac{7}{8}$
$\frac{3}{8}$
32
-(8) 3/8"-16 BOLTS WITH WING NUTS EQ. SPACED ON 21 1/2" B.C.
$2\frac{1}{2}$"
7" O.D.
$\frac{1}{8}$
$1\frac{1}{2}$
$8\frac{1}{2}$"
10
$17\frac{1}{2}$
33"
36"
$6\frac{3}{4}$
$3\frac{1}{4}$"
$14\frac{1}{2}$"
GE POLYDYNE DRIVE (SEE NOTE 2)
NOTES
1. ALL CONTACT MATERIAL TO BE: CARBON STEEL
2. MOTOR TO BE 1/3 HP, TEFC., 230-460/3/60
MATERIAL PULVERIZED COAL
BULK DENSITY 40 LBS/FT³
FLOW RATE 2-20 LBS/HOUR
MOISTURE CUST. TO ADVISE
TEMPERATURE CUST. TO ADVISE
PRESSURE 5 PSI
Vibra Screw Feeders, Inc.
755 UNION BLVD TOTOWA N.J. 07512
TITLE 5/8" LIVE BIN FEEDER FOR
FOR: PRINCETON CHEMICAL RESEARCH INC.
DATE 6-12-70 F.H
CHK. BY
APP. BY
SCALE NONE
DWG NO F681652
DO NOT SCALE PRINT

FIGURE IV-13 NATURAL GAS BOOSTER ENGINEERING DRAWING


REPRO OF 830-796-022
2'-1
G
15 5/16
3 11/16
5 1/8
6 1/2
6 7/8
7 1/2
14
4
17
8 1/8
7 1/16
3/4 PIPE TAP-
INLET
COUPLING GUARD
1/8
1 7/8
1 7/8
11 7/8
5
8
3
5 7/8
1 1/2
GROUT
7 3/8
15 5/16
5 7/8
2'-4 7/16
3 1/4
4 1/2
11 1/8
3/8 BOLTS IN 1 1/2 PIPES-
NOT FURN. BY ROOTS
3/4 PIPE TAP-
DISCHARGE
20T20 FALK
COUPLING
1 3/4
1 3/4
7 3/4
6 1/4
14
1 BEDPLATE 846-898-021 ST'L
1 GUARD COUPLING 887-189-020 ST'L
4 CAPSCREW, BLR MTG 810-019-004 5/8-16-1 5/8 LG ST'L
4 CAPSCREW, MTR MTG 810-019-004 5/8-16-1 3/8 LG ST'L
4 CAPSCREW, GRD MTG 810-011-001 1/4-20-1/2 LG ST'L
1 COUPLING, FALK 20T20
2 HP., 1750 RPM, 3PH., 60 CYC., 230/460 VOLT
FRAME 145T T.E.F.C. ELECTRIC MOTOR.
CERTIFIED FOR
CUST. ORDER
OUR ORDER
BY
ROOTS-CONNERSVILLE BLOWER
DO NOT SCALE FOR DIMENSIONS
315 TYPE XA GAS PUMP
ELECTRIC MOTOR DRIVEN
ROOTS-CONNERSVILLE BLOWER
CONNERSVILLE, INDIANA
N.T.S
846391-022
5-6770

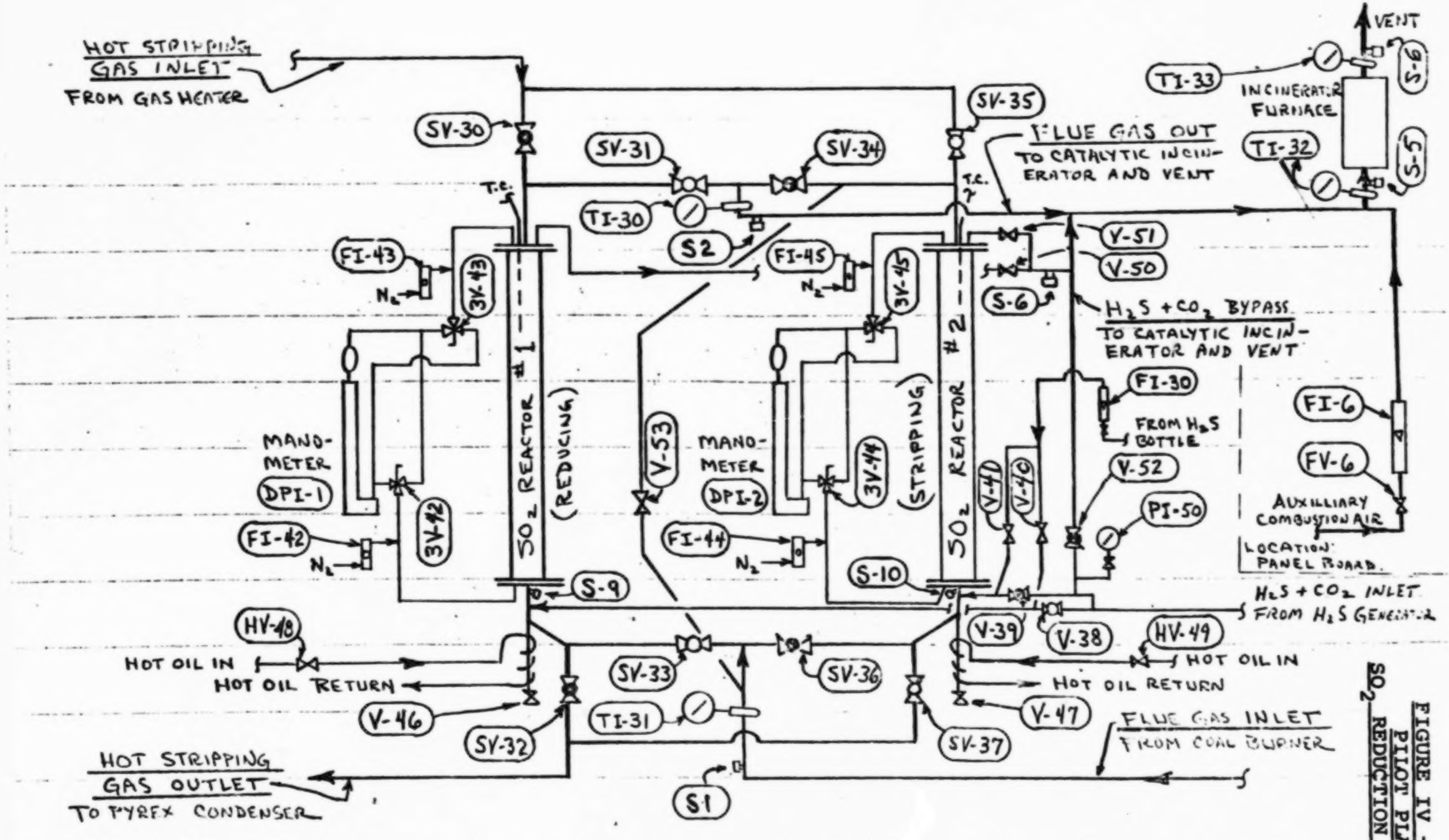

HOT STRIPPING GAS INLET
FROM GAS HEATER
SV-30
SV-31
SV-34
SV-35
T.C.
T.C.
TI-30
S2
FLUE GAS OUT
TO CATALYTIC INCINERATOR AND VENT
TI-33
INCINERATOR FURNACE
VENT
S-6
S-5
TI-32
FI-43
N_2
3V-43
V-51
V-50
S-6
FI-45
N_2
3V-45
$H_2S + CO_2$ BYPASS
TO CATALYTIC INCINERATOR AND VENT
FI-30
FROM H_2S BOTTLE
FI-6
FV-6
AUXILLIARY COMBUSTION AIR
LOCATION: PANEL BOARD.
MANOMETER
DPI-1
3V-42
FI-42
N_2
SO_2 REACTOR #1
(REDUCING)
V-53
MANOMETER
DPI-2
3V-44
FI-44
N_2
(STRIPPING)
SO_2 REACTOR #2
V-41
V-40
V-52
PI-50
S-9
S-10
$H_2S + CO_2$ INLET
FROM H_2S GENERATOR
HV-48
HOT OIL IN
HOT OIL RETURN
SV-33
SV-36
V-39
V-38
HV-49
HOT OIL IN
HOT OIL RETURN
V-46
SV-32
TI-31
SV-37
V-47
FLUE GAS INLET
FROM COAL BURNER
HOT STRIPPING GAS OUTLET
TO PYREX CONDENSER
S1

FIGURE IV - 14
PILOT PLANT
SO_2 REDUCTION SYSTEM

FIGURE IV - 15

PILOT PLANT SULFUR STRIPPING SYSTEM

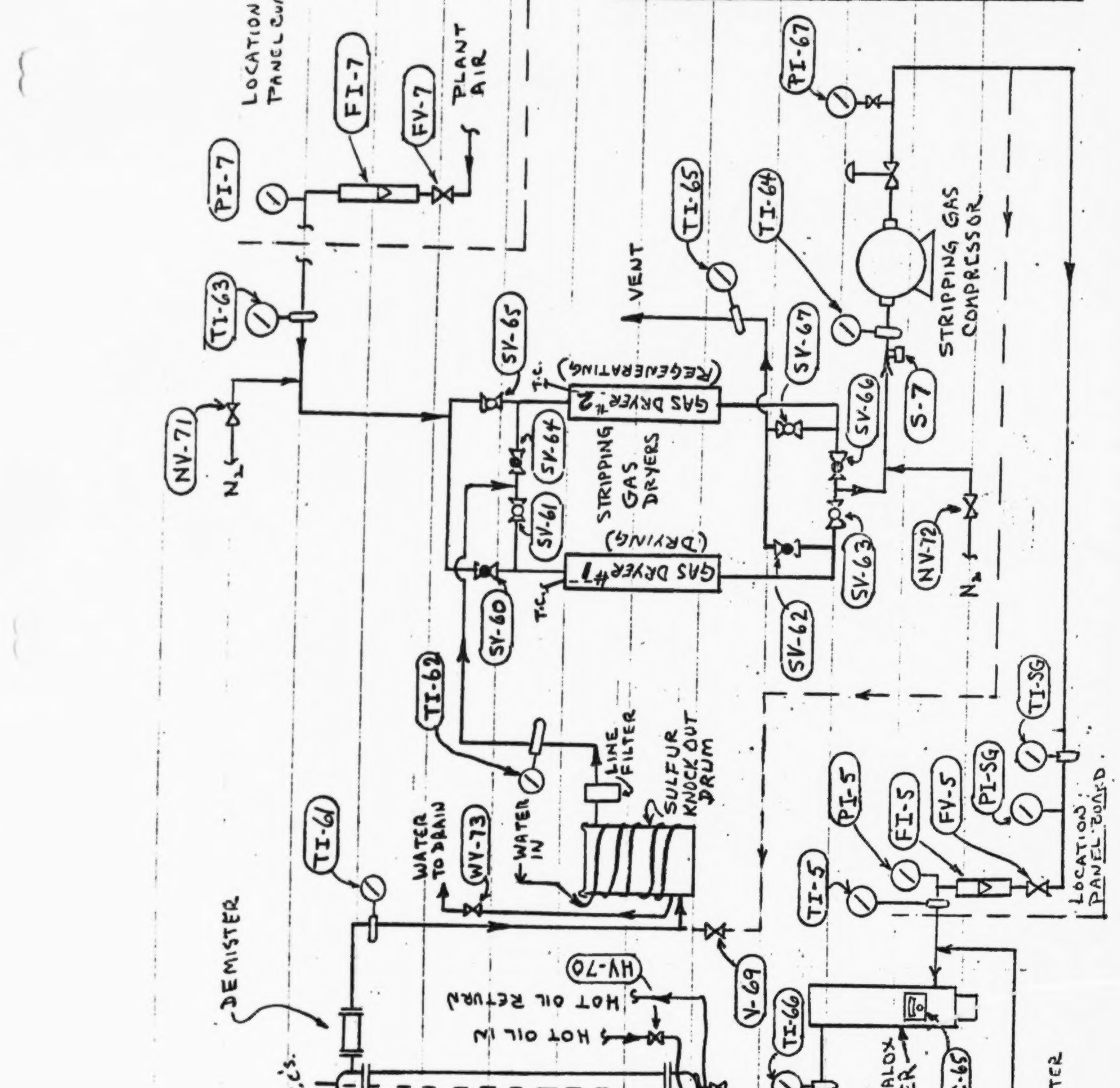
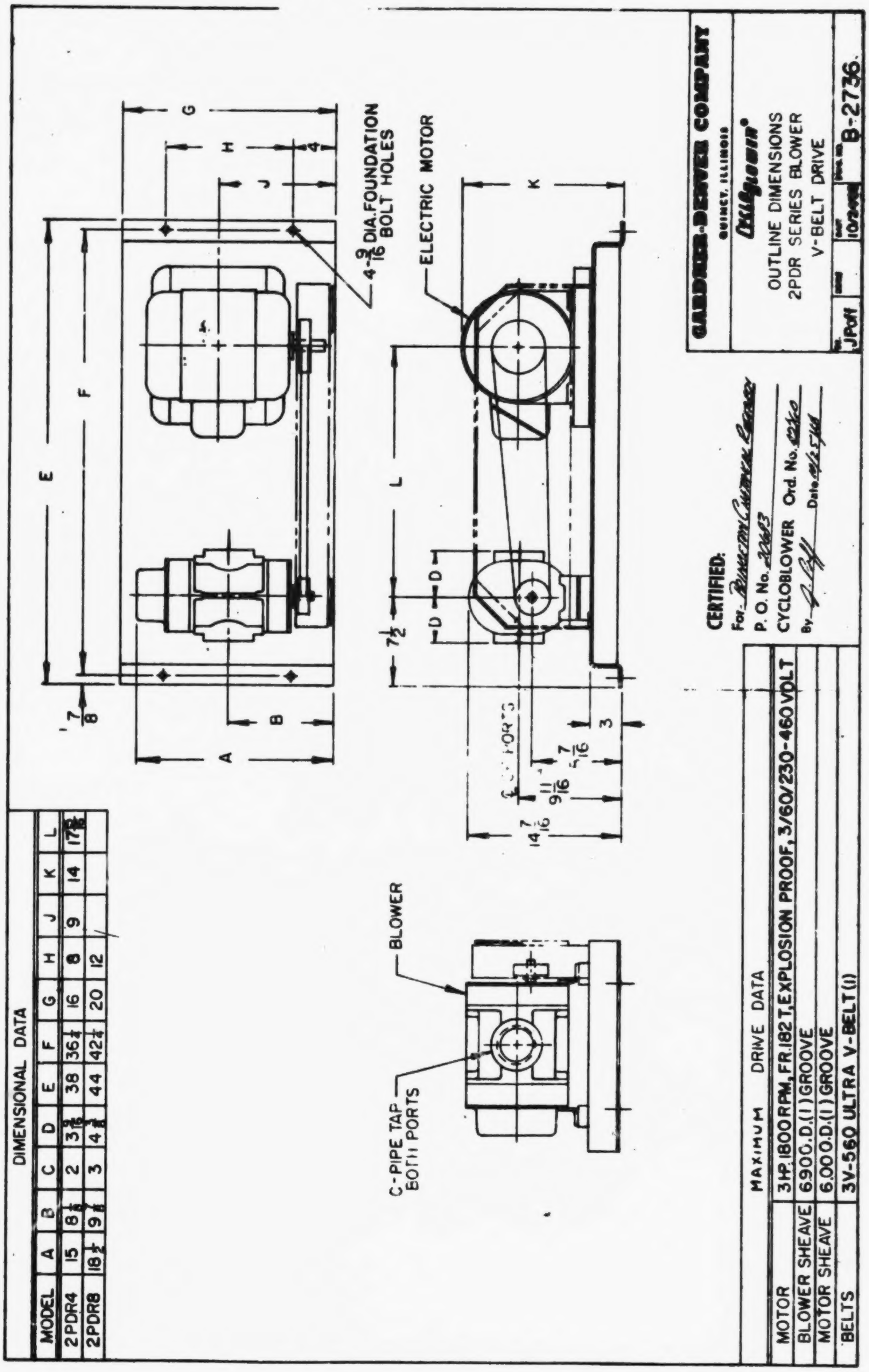

LOCATION: PANEL BOARD
PI-7
FI-7
FV-7
PLANT AIR
TI-63
NV-71
N2
SV-65
T.C.
GAS DRYER #2
(REGENERATING)
SV-64
SV-61
STRIPPING GAS DRYERS
GAS DRYER #1
(DRYING)
SV-60
T.C.
VENT
TI-65
SV-67
SV-66
SV-63
SV-62
NV-72
N2
TI-64
S-7
STRIPPING GAS COMPRESSOR
PI-67
TI-62
LINE FILTER
SULFUR KNOCK OUT DRUM
WATER TO DRAIN
WV-73
WATER IN
TI-61
DEMISTER
T.C'S.
SULFUR CONDENSER
HOT OIL IN
HOT OIL RETURN
HV-70
V-69
V-68
TI-60
STRIPPING GAS FROM REACTORS
TI-66
STRIPPING GAS TO REACTORS
CHROMALOX HEATER
TC-65
TI-5
PI-5
FI-5
FV-5
PI-SG
TI-SG
LOCATION: PANEL BOARD
HUMIDIFIER WATER PUMP
BURETTE

FIGURE IV-16 STRIPPING GAS BLOWER ENGINEERING DRAWING


E
F
$\frac{7}{8}$
A
B
G
H
J
4
$4\text{-}\frac{9}{16}$ DIA. FOUNDATION BOLT HOLES
C-PIPE TAP BOTH PORTS
BLOWER
ELECTRIC MOTOR
$7\frac{1}{2}$
L
D
D
K
℄ OF PORTS
$14\frac{7}{16}$
$9\frac{11}{16}$
$5\frac{7}{16}$
3

DIMENSIONAL DATA											
MODEL	A	B	C	D	E	F	G	H	J	K	L
2PDR4	15	$8\frac{1}{8}$	2	$3\frac{9}{16}$	38	$36\frac{1}{4}$	16	8	9	14	$17\frac{3}{16}$
2PDR8	$18\frac{1}{2}$	$9\frac{7}{8}$	3	$4\frac{3}{8}$	44	$42\frac{1}{4}$	20	12			

	MAXIMUM DRIVE DATA
MOTOR	3HP, 1800 RPM, FR. 182T, EXPLOSION PROOF, 3/60/230-460 VOLT
BLOWER SHEAVE	6.90 O.D. (1) GROOVE
MOTOR SHEAVE	6.00 O.D. (1) GROOVE
BELTS	3V-560 ULTRA V-BELT (1)

CERTIFIED:
For Princeton Chemical Research
P. O. No. 20683
CYCLOBLOWER Ord. No. [illegible]
By J. Poff Date [illegible]

GARDNER-DENVER COMPANY
QUINCY, ILLINOIS
CYCLOBLOWER®
OUTLINE DIMENSIONS
2PDR SERIES BLOWER
V-BELT DRIVE
JPoff
10/24/68
B-2736

FIGURE IV - 17

PILOT PLANT H_2S GENERATION SYSTEM

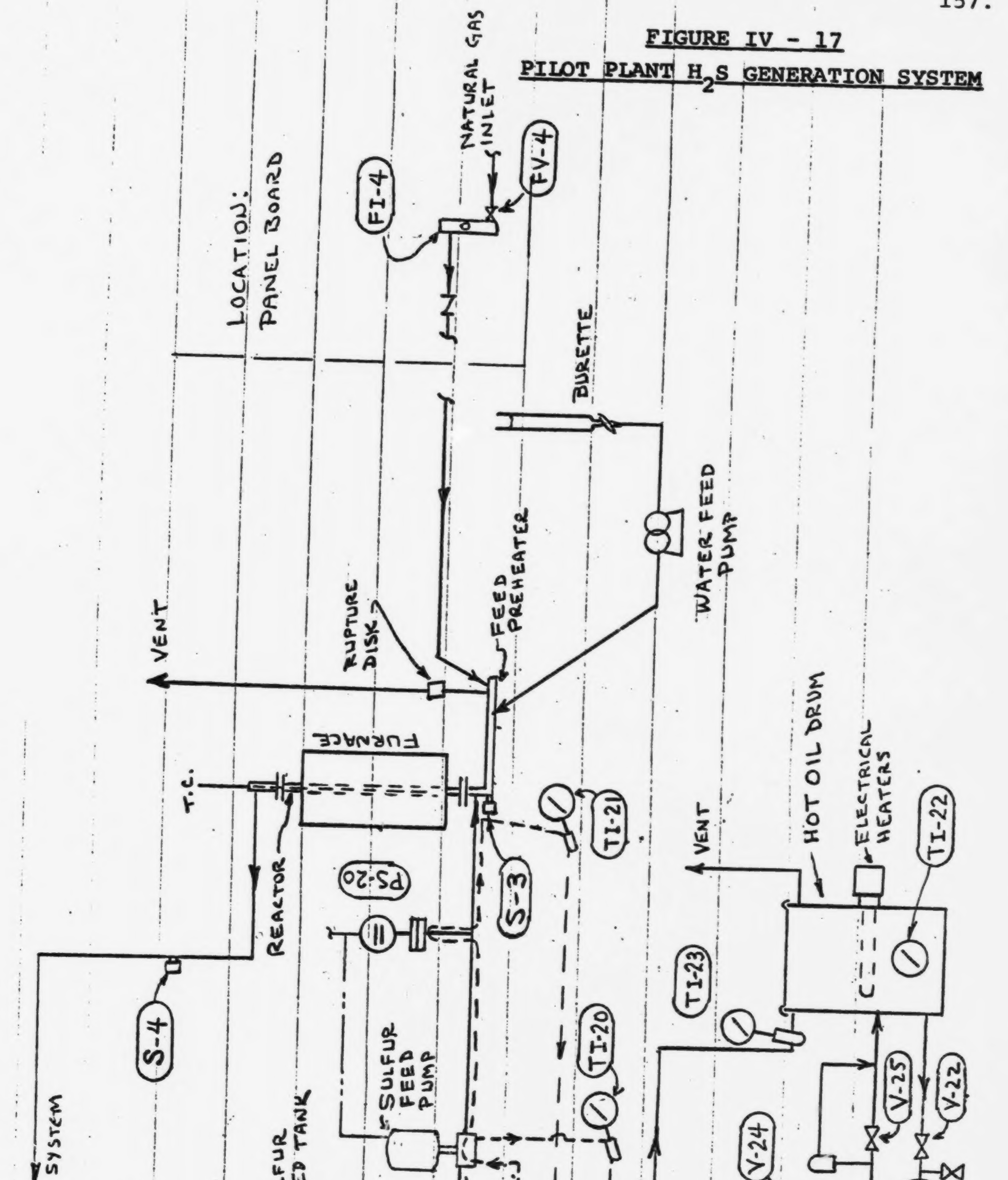
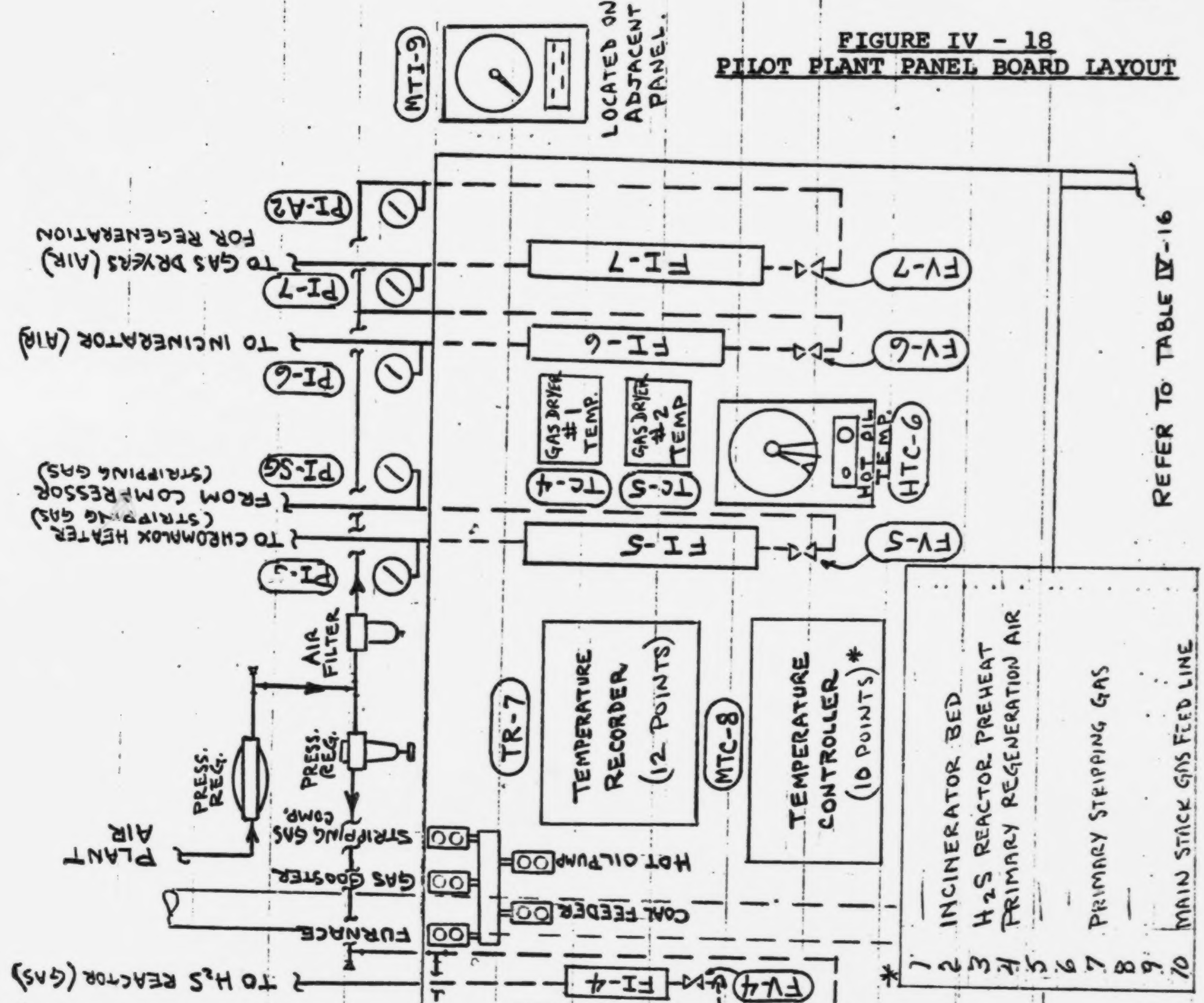

LOCATION: PANEL BOARD
NATURAL GAS INLET
FV-4
FI-4
BURETTE
WATER FEED PUMP
FEED PREHEATER
RUPTURE DISK
VENT
FURNACE
T.C.
REACTOR
S-3
TI-21
PS-20
S-4
SULFUR FEED PUMP
SULFUR FEED TANK
TI-20
HV-21
HV-20
VENT
HOT OIL DRUM
ELECTRICAL HEATERS
TI-22
TI-23
V-25
V-22
V-24
V-23
V-26
V-27
PI-24
HOT OIL PUMP
TO SO_2 RCTRS. & SULFUR COND.
$H_2S + CO_2$ OUTLET TO SO_2 REDUCTION SYSTEM

FIGURE IV - 18
PILOT PLANT PANEL BOARD LAYOUT


MTI-9
LOCATED ON ADJACENT PANEL
PI-A2
PI-7
PI-6
PI-SG
PI-5
TO GAS DRYERS (AIR) FOR REGENERATION
TO INCINERATOR (AIR)
FROM COMPRESSOR (STRIPPING GAS)
TO CHROMALOX HEATER (STRIPPING GAS)
AIR FILTER
PRESS. REG.
PRESS. REG.
PLANT AIR
STRIPPING GAS COMP.
GAS BOOSTER
FURNACE
HOT OIL PUMP
COAL FEEDER
FI-7
FI-6
FI-5
FI-4
FI-3
FI-2
FI-1
FV-7
FV-6
FV-5
FV-4
FV-3
FV-2
FV-1
GAS DRYER #1 TEMP.
TC-4
GAS DRYER #2 TEMP
TC-5
HOT OIL TEMP.
HTC-6
TR-7
TEMPERATURE RECORDER (12 POINTS)
MTC-8
TEMPERATURE CONTROLLER (10 POINTS)*
*
1 INCINERATOR BED
2 H2S REACTOR PREHEAT
3 PRIMARY REGENERATION AIR
4
5
6 PRIMARY STRIPPING GAS
7
8
9
10 MAIN STACK GAS FEED LINE
REFER TO TABLE IV-16
TO H2S REACTOR (GAS)
TO COAL BURNER (AIR)
TO COAL BURNER (AIR)
TO COAL BURNER (GAS)
FROM GAS BOOSTER (GAS)
PI-3
PI-2
PI-1
PI-G
PI-A1
STRIPPING GAS H.T. CUTOFF
TA-9
SO2 RCTR #1 TEMP.
TC-1
SO2 RCTR #2 TEMP.
TC-2
H2S RCTR BED TEMP.
TC-3
OXYGEN MONITOR
CI-10

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION V

PROCESS DESIGN AND ECONOMICS

TABLE OF CONTENTS

SECTION V - PROCESS DESIGN AND ECONOMICS

Page

1. Process Design - 1400 Megawatt Power Plant 164
   1.1 Process Description 164
   1.2 Design Basis 165
   1.3 Equipment Design and Pricing 168
   1.4 Utility Requirements 168
2. Projected Economics - 1400 Megawatt Power Plant 168
   2.1 Investment Cost Determination 169
   2.2 Operating Cost Determination 169
   2.3 Sensitivity of Economics 169
      2.31 Sulfur Content of the Coal 170
      2.32 Power Plant Size 170
      2.33 Operating Factor 170
      2.34 Catalyst Costs 171
   2.4 Attractive Economic Circumstances 171
3. Preliminary Economic Comparisons - Conceptual Designs 172
   3.1 Process Alternatives - 800 Megawatt Power Plant 172
   3.2 Economic Comparison With Advanced SO_2 Removal Processes 173
   3.3 Economics of Process Applied to Smelting Plant 174
   3.4 Design Basis 174

LIST OF TABLES

SECTION V - PROCESS DESIGN AND ECONOMICS

Table	Title	Page
V-1	Material Balance For 1400 Megawatt Power Plant	175
V-2	Major Equipment List For 1400 Megawatt Power Plant	177
V-3	Investment Cost Determination For 1400 Megawatt Power Plant	178
V-4	Operating Costs For 1400 Megawatt Power Plant	179
V-5	Preliminary Investment and Operating Costs For 800 Megawatt Power Plant - Conceptual Designs	180
V-6	Preliminary Capital Requirements for 800 Megawatt Power Plant - Conceptual Designs	181
V-7	Prelininary Operating Costs For 800 Megawatt Power Plant - Conceptual Designs	182
V-8	Comparison of Preliminary Investment and Operating Costs For 800 Megawatt Power Plant with Advanced Processes	183
V-9	Comparison of Preliminary Capital Requirements For 800 Megawatt Power Plant With Advanced Processes	184
V-10	Comparison of Preliminary Operating Costs For 800 Megawatt Power Plant With Advanced Processes	185

LIST OF TABLES (Cont.)

SECTION V - PROCESS DESIGN AND ECONOMICS

Table	Title	Page
V-11	Preliminary Investment and Operating Costs For 1630 Tons/Day Copper Ore Smelter - Conceptual Design	187
V-12	Preliminary Capital Requirements For 1630 Tons/Day Copper Ore Smelter - Conceptual Design	188
V-13	Preliminary Operating Costs For 1630 Tons/Day Copper Ore Smelter - Conceptual Design	189
V-14	Bases Used In Preliminary Economic Evaluation-Conceptual Designs	190

LIST OF FIGURES

SECTION V - PROCESS DESIGN & ECONOMICS

Figure	Title	Page
V-1	Final Process Flowsheet For Switching Fixed Bed Concept of PCR Process	195
V-2	Conceptual Design - Fixed Bed Steady State Process For Power Plant	196
V-3	Conceptual Design - Switching Fixed Bed Process For Power Plant	197
V-4	Conceptual Design - Fixed Bed Steady State Process for Power Plant CS_2 Reductant	198
V-5	Conceptual Design - Fluid Bed Steady State Process For Power Plant	199
V-6	Conceptual Design - Fluid Bed Steady State Process For Power Plant	200
V-7	Conceptual Design - Fixed Bed Steady State Process For Copper Ore Smelter	201
V-8	Conceptual Design - Switching Fixed Bed Process For Copper Ore Smelter	202

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION V - PROCESS DESIGN AND ECONOMICS

1. Process Design - 1400 Megawatt Power Plant

A process design was carried out for a new 1400 megawatt power plant producing 2.5 million standard cubic feet per minute of flue gas containing 0.3% SO_2. Since so little pilot plant data were obtained, the design was based largely on the bench scale work and known engineering principles.

The switching fixed bed approach was chosen for this design, although a fluid bed design may have advantages. The process is represented by flowsheet, Figure V-1. Table V-1 is a material balance for the process.

The design is based on activated alumina catalyst, which will not function well in the presence of nitrogen oxides. The economics will have to be adjusted as in paragraph 2.34, unless the nitrogen oxides are removed or reduced prior to the reactors, or the alumina can be modified to perform in their presence.

1.1 Process Description

The flue gas from the electrostatic precipitator, at 300°F, is compressed and cooled to 230°F by the adiabatic vaporization of water sprayed into the gas. The reducing gas, rich in H_2S, is added to the flue gas and the mixture is passed through the reducing reactors, where the H_2S and SO_2 react to form sulfur which is deposited on the catalyst. The gas leaving the reducers is then vented to the stack.

After about 10 hours on-stream (catalyst loading about 25%), the reducing reactors are then switched to regeneration, where they are heated up to remove sulfur, cooled, and returned to stand-by for reduction within about 9 hours. Four stacks of reactors are provided, two on reduction, one on heating, one on cooling. By recirculating the stripping gas through the latter two in series, a major portion of the heating requirements of one can be provided from the one being cooled. A fired heater is provided for the balance of the heating. Cooling of the gas and sulfur condensation is accomplished by molten sulfur scrubbing with a cooler on the recirculating sulfur.

Hydrogen sulfide reducing gas is produced by passing a mixture of sulfur, water, and natural gas through a catalytic reactor at high temperature. The preheat and vaporizing heat requirements are provided by injection of hot combustion gases. An excess of natural gas in this combustion eliminates oxygen, and provides part of the methane requirements of the reaction. Part of the water required is also provided from the combustion gases. The reducing gases are adiabatically cooled prior to mixing with flue gas.

1.2 Design Basis

(a) New Power Plant - 1400 M.W. burning 580 tons/hour of coal, producing a 2.5 MM SCFM (70°F, 760 mm Hg) flue gas, and operating 330 days/year at 100% capacity.

(b) Flue gas:

N_2	74.89 mole %	SO_2	0.3
O_2	2.8	SO_3	0.01
CO_2	14.7	NO_x	0.05
H_2O	7.25		

Temperature:

300°F (downstream of electrostatic precipitator)

(c) H_2S generator - based on Run 322 (original Run No. 32), adjusted for material balance:

Catalyst: Activated Alumina

Contact Time: 9 seconds

Temperature: 1319°F

Molar Rates (Relative to input methane):

Compound	In	Out
S_2	2.08	0.26
CH_4	1.00	0.06
H_2O	3.54	1.80
H_2S	-	3.62
CO_2	-	0.80
COS	-	0.02
CS_2	-	0.00
CO	-	0.12

and diluted with combustion gases.

(d) Reducing Conditions:

Catalyst: Activated Alumina
Contact Time: ~2 seconds (1800 space velocity)
Particle Size: ~1 inch (requires confirmation)
Temperature: 230°F
H_2S/SO_2 Ratio = 2.0/1.0
H_2S/SO_3 Ratio = 3.0/1.0

(e) Reduction Performance:

- SO_2, H_2S conversions set by equilibrium (bench data indicate higher conversions are achieved)
- 100% SO_3 conversion (requires confirmation)
- Sulfur vapor pressure reduced by adsorption to about 10% of normal vapor pressure
- CO, COS, CH_4 unreacted (requires investigation)
- 94% SO_2 removal
- 92% sulfur recovery

(f) Residual Gas Composition:

	Flue Gas After Reduct. ppm (c)	Average(b) Ground Level Conc. ppm (c)	Maximum(b) Ground Level Conc. ppm (c)	Thresh-(a) old Toxic Level	Thresh-(a) old Odor Level
CH_4	100	.010	.050	33%	odorless
CO	200	.020	.100	50 ppm	odorless
COS	25	.002	.013	?	?
SO_2	165	.017	.083	5 ppm	0.3-0.9 ppm
H_2S	44	.004(d)	.022(d)	10 ppm	$\leq$.032(d) ppm
S_8	1.9	0.0002	0.0008	"very low"	?
CS_2	Neg.	Neg.	Neg.	20 ppm	nearly odorless

(a) From "Properties of Dangerous Materials" by I. Sax.

(b) From "Air Quality Criteria" 1965 and "The Tall Stack", typical dispersion factors are 2000-50,000. Arbitrarily use 10,000 factor for average ground level concentration, and 2,000 factor for maximum ground level concentration.

(c) Volumetric

(d) Typical permissible standards = 0.10-0.24 ppm (NAPCA Publication No. APTD 69-37)

The above data show the concentration of trace compounds possibly remaining in the flue gas to be at acceptable levels, below both threshold odor and toxic levels.

(g) Reducing Reactor Design:

Mass flow rate: 836 lb./hr.-ft.^{2}
Superficial Velocity: 4.0 ft./sec.
On-stream Time: ~10 hours
Maximum allowable reactor diameter: ~50 feet

(h) Stripping and Catalyst Reactivation:

5% H_2S in N_2 recycle gas
Temperature: 1000°F
Rate sufficient to heat beds by direct contact with hot recycle gas in 5 hours (cooling ~4 hours)
Sulfur recovery by molten sulfur scrubbing of recycle gas

1.3 Equipment Design and Pricing

Table V-2 lists the sizes, prices, and utility requirements of all the major equipment items. Quotes were obtained on several items. The reactors were priced from vessel cost curves, and a 35% uncertainty factor was applied. Because of the large size of these reactors, and the expansion effects of the temperature cycling, further work is required to firm up these costs. The balance of the equipment is believed to be well defined.

Duct-work and valving are believed to be major costs, but were assumed to be covered by the cost factors presented in Table V-3. Further work is required.

1.4 Utility Requirements

Utility requirements for all the equipment are listed in Table V-2 and summarized in Table V-4 (Operating Costs).

2. Projected Economics - 1400 Megawatt Power Plant

The projected economics of the process are based on the process design previously outlined. For a new 1400 M.W. power plant burning 4.5% S coal (0.3% SO_2 flue gas), and operating at 100% capacity, 330 days/year, an investment of $11,400,000 ($8.15/KW) is projected. Operating costs of $4,577,000/year (or $33/ton sulfur produced) are indicated.

2.1 Investment Cost Determination

The capital cost requirements were developed by factors on the basic equipment costs. Table V-3 summarizes the factors used and applied to this case. The following key costs have been extracted from the table:

Purchased Equipment	$2.91 MM
Physical Plant Costs (Including offsites)	7.80 MM
Direct Plant Costs (Including engineering and construction)	8.70 MM
Fixed Capital Costs (Including contingency)	9.40 MM
Total Investment (Including interest, working capital and initial catalyst charge)	11.40 MM

2.2 Operating Cost Determination

Operating costs were determined on the basis of the NAPCA guidelines. Table V-4 summarizes the five operating cost categories:

Raw Materials	$210,000/year
Utilities	2,128,000
Labor	146,000
Operations	871,000
Capital Charges	1,222,000
	$4,577,000/year

2.3 Sensitivity of Economics

The economics are particularly sensitive to:

(a) Sulfur content of the coal
(b) Plant Size
(c) Operating Factor
(d) Catalyst cost

2.31 Sulfur Content of the Coal

For the 1400 M.W. power plant with a 90$^+$% operating factor, the following investments and operating costs are indicated for various coals:

% S Coal	% SO_2 Gas	Investment Required	Operating Costs		
			$/year	$/ton coal	$/ton sulfur
3.0	0.2	$10,700,000	$3,830,000	$0.83	$41
4.5	0.3	11,400,000	4,577,000	1.00	33
6.0	0.4	12,100,000	5,390,000	1.17	28

Clearly, high sulfur coal should be sought to increase breakeven possibilities.

2.32 Power Plant Size

The major effect of the plant size is on the investment and capital charges. Assuming the investment varies in proportion to the 0.7 power of the capacity ratio, the following sets of economics are indicated. The 90$^+$% operating factor and 4.5% coal are assumed.

Plant Size M.W.	Investment		Operating Costs		
	$	$/KW	$/year	$/ton coal	$/ton sulfur
1400	$11,400,000	$8.15	$4,577,000	$1.00	$33
1000	8,900,000	8.90	3,500,000	1.07	35
600	6,200,000	10.30	2,400,000	1.20	40
200	2,800,000	14.00	1,100,000	1.66	55

2.33 Operating Factor

A low operating factor reduces the amount of sulfur by-product, while the fixed costs (capital charges, labor, overhead, etc.) remain the same. In a 1400 M.W. plant burning 4.5% S coal, the following effects of operating factor may be expected (Maintenance and catalyst replacement cost have been assumed to be a fixed cost/year regardless of operating factor).

Operating Factor %	Operating Costs $/year	Operating Costs $/ton sulfur
100	$4,810,000	$32
90	4,580,000	33
70	4,100,000	38
50	3,630,000	48

2.34 Catalyst Costs

The process design and economics presented above were based on large volume activated alumina catalyst prices of $0.12/lb. which were quoted by Alcoa. Molecular sieve prices in very large quantities (1-10 MM lbs.) have been quoted (by Linde) at $.75/lb., although private studies (not at PCR) indicate $0.25/lb. could be reached. If the molecular sieves were found to be the only suitable catalyst in the presence of NO_x, the above economics (1400 M.W., 0.3% SO_2, 90% factor) would change as follows (unless the sieves performed better, e.g., had a longer life).

	Activated Alumina Catalyst @ $0.12/lb.	Molecular Sieve(13X) @ $0.25/lb.	Molecular Sieve(13X) @ $0.75/lb.
Investment:	$11,400,000	$12,600,000	$17,200,000
Operating Costs:	$4,577,000	$4,800,000	$5,700,000
$/ton coal	$1.00	$1.05	$1.23
$/ton sulfur	$33	$34	$41

2.4 Attractive Economic Circumstances

The process becomes very economically attractive if a source of H_2S is available, such as from a refinery or natural gas sweetening plant. If H_2S need not be generated, the economics change as follows (assuming the H_2S is received at no cost by returning elemental sulfur to the source at no cost). A 1400 M.W. plant burning 4.5% S coal, 330 days at 100% capacity is assumed:

Investment	Operating Costs $/year	Operating Costs $/ton coal	Operating Costs $/ton sulfur
$11,000,000	$3,310,000	$0.72	$24

One other interesting situation would be where the power company would provide the capital investment for the sulfur recovery plant, and incorporate the capital charges into its rate structure as an air pollution abatement cost. This then would make the sulfur plant attractive for a chemical company to operate. On the same basis as above, the economics then are:

Investment	Capital Charges to Power Company $/year	 $/ton coal	Sulfur Production Cost To Plant Operator $/ton sulfur
$11,400,000	$1,232,000	$0.27	$24

3. Preliminary Economic Comparisons - Conceptual Designs

Early in the program, comparisons of various process alternatives were made to pinpoint the most promising approach to pilot. Other more advanced processes were compared to define the incentive for continued work.

Five variations of the process for power plant application were considered. It should be noted that these studies were made relatively early in the program, and contain assumptions* which later proved to be false. No significance is attached to these studies other than to point out the possible economic merits of the alternates.

Although the studies require refining, no attempt to do so was made. The switching fixed bed approach has advantages, but these must be compared again with the fluid bed approaches. Case 3 has been shown to be academic, as CS_2 is not reactive in the flue gas temperature range.

3.1 Process Alternatives - 600 Megawatt Power Plant

Five variations of the process were considered:

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* For example, oxygen has been assumed to be unreactive under Claus process conditions at 392 and 600°F. Oxygen was later shown at least partly to react with H_2S and CS_2 under these conditions.

Case	Reductant	Reactor Concept	SO_2 Removal
1.	H_2S	Steady State Fixed Bed	80%
2.	H_2S	Switching Fixed Bed	98%
3.	CS_2	Steady State Fixed Bed	90%
4.	H_2S	Steady State Fluid Bed (Catalyst cycling between SO_2 reducer and H_2S generator)	98%
5.	H_2S	Steady State Fluid Bed (Catalyst cycling between SO_2 reducer and sulfur stripping)	98%

The process economics were prepared on the same basis used by Katell (CEP, Vol. 62, No. 10, p. 67, 1966). Table V-5 summarizes the investment and operating costs for these five cases. Tables V-6, 7 are a more detailed breakdown of these costs. Figures V-2, 3, 4, 5, 6 are flowsheet-material balance diagrams for the five cases.

Case 2, the switching fixed bed concept projected the best economics, and was chosen to be the pilot plant concept.

3.2 Economic Comparison With Advanced SO_2 Removal Processes

To define the economic prospects for the process, Case 2 was compared with the Alkalized Alumina, Reinluft, and Catalytic Oxidation Processes on the basis defined by Katell. Although in a much earlier stage of development, the process appeared to have potentially better operating economics.

Table V-8 is a summary of the economic comparison, including investment and operating costs. Tables V-9, 10 are more detailed cost breakdowns.

3.3 Economics of Process Applied to Smelting Plant

The process was evaluated for application to a 1630 ton perday copper ore smelting plant with a 2% SO_2 concentration in the tail gas. Two cases were studied: steady state fixed bed and switching fixed bed reactors; H_2S reductant. Figures V-7, 8 are flowsheet-material balance diagrams for these cases.

As shown in Tables V-11, 12, 13 the process has potential for this application also.

3.4 Design Basis

Table V-14 lists the bases and assumptions used in this preliminary economic study.

TABLE V-1

MATERIAL BALANCE

1400 M.W. Power Plant, 2.5 MM SCFM, 0.3% SO_2, Ash Free Flue Gas

	Flue Gas		Reducing Stream		"Flue Gas" to Adiab. Cooling		Total H_2O Spray Coolant		Feed to SO_2 Reactor		Sulfur Knock Out	
	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.
N_2	29.065	813.8	0.2464	6.9	29.311	820.7	-	-	29.311	820.7	-	-
O_2	1.087	34.8	-	-	1.087	34.8	-	-	1.087	34.8	-	-
CO_2	5.705	251.0	0.0841	3.7	5.789	254.7	-	-	5.789	254.7	-	-
H_2O	2.814	50.6	0.1158	2.1	2.930	52.7	1.368	24.6	4.298	77.3	-	-
SO_2	0.116	7.4	-	-	0.116	7.4	-	-	0.116	7.4	-	-
SO_3	0.004	0.3	-	-	0.004	0.3	-	-	0.004	0.3	-	-
H_2S	-	-	0.2329	7.9	0.233	7.9	-	-	0.233	7.9	-	-
"S"	-	-	0.0335	1.1	0.034	1.1	-	-	0.006	0.2	0.028	0.9
COS	-	-	0.0013	<0.1	0.001	<0.1	-	-	0.001	<0.1	-	-
NO_x	0.019	0.7	-	-	0.019	0.7	-	-	0.019	0.7	-	-
CH_4	-	-	0.0039	<0.1	0.004	<0.1	-	-	0.004	<0.1	-	-
CO	-	-	0.0077	0.2	0.008	0.2	-	-	0.008	0.2	-	-
Total	38.810	1158.6	0.7256	22.1	39.536	1180.7	1.368	24.6	40.876	1204.4	0.028	0.9

- See Figure V-1
- Actual Flows Have Been Multiplied By 10^{-4}

TABLE V-1 (Cont.)

MATERIAL BALANCE

1400 M.W. Power Plant, 2.5 MM SCFM, 0.3% SO_2, Ash Free Flue Gas

	SO_2 Reactor Effluent		H_2S Generator Feed		H_2S Generator Effluent		Sulfur on Catalyst		Sulfur Product	
	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.	lb mol/ hr.	lb/hr.
N_2	29.311	820.7	0.2464	6.9	0.2464	6.9	-	-	-	-
O_2	1.087	34.8	-	-	-	-	-	-	-	-
CO_2	5.789	254.7	0.0318	1.4	0.0841	3.7	-	-	-	-
H_2O	4.527	81.2	0.2278	4.1	0.1158	2.1	-	-	-	-
SO_2	0.007	0.4	-	-	-	-	-	-	-	-
SO_3	tr.	-	-	-	-	-	-	-	-	-
H_2S	0.002	< 0.1	-	-	0.2329	7.9	-	-	-	-
"S"	0.0006	0.02	0.2677	8.7	0.0335	1.1	0.3491	11.2	0.1094	3.5
COS	0.001	<0.1	-	-	0.0013	<0.1	-	-	-	-
NO_x	0.019	0.7	-	-	-	-	-	-	-	-
CH_4	0.004	<0.1	0.0643	1.0	0.0039	<0.1	-	-	-	-
CO	0.008	0.2	-	-	0.0077	0.2	-	-	-	-
Total	40.756	1193.2	0.8380	22.1	0.7256	22.1	0.3491	11.2	0.1094	3.5

- See Figure V-1
- Actual Flows Have Been Multiplied By 10^{-4}

TABLE V-2. MAJOR EQUIPMENT LIST

1400 M.W. POWER PLANT — 330 DAYS AT 100% CAPACITY — 0.3% SO_2 FLUE GAS.

DESIGNATION	DESCRIPTION	NO.	SIZE + MATERIALS OF CONSTRUCTION	PURCHASE COST	SOURCE OF COST	UTILITY REQUIREMENTS
FANS						
C-1	FLUE GAS FANS (incl. MOTORS)	5	500,000 CFM, 15" H_2O ΔP, MILD STEEL	$ 395,000	BUFFALO FORGE CO.	5600 KWH/Hr
C-2	STRIPPING GAS BLOWER (")	2	85,000 CFM, 55" H_2O ΔP, EPOXY COATED STEEL	81,000	BUFFALO FORGE CO.	1680 KWH/Hr
REACTORS						
R-1,2,3,4	REDUCING REACTORS	4	5½'D x 50' STAINLESS VESSELS, 3 CATALYST BEDS/VESSEL	1,900,000	COST CURVES + 35%	8.56 MM lbs CATALYST CHARGE
R-5	H_2S GENERATOR	1	12'D x 30' REFRACTORY LINED MILD STEEL VESSEL	25,000	COST CURVES	0.17 " " " " 10,000 lbs [illegible] CH_4, 29,000 Kg/Hr H_2O
FURNACES						
F-1	STRIPPING GAS HEATER	1	20 MM BTU/Hr DIRECT FIRED HEATER, ALLOY TUBES	100,000	COST CURVES	25 MM BTU/Hr
F-2	H_2S GENERATOR PREHEATER	1	104 MM BTU/Hr HOT COMBUSTION GAS GENERATOR	50,000	COST CURVES	104 MM BTU/Hr
VESSELS						
T-1	FLUE GAS COOLING CHAMBER	1	450,000 GALLON "EPOXY" COATED MILD STEEL	70,000	COST CURVES	} 500 gpm @ 70°F
T-2	REDUCING GAS COOLING CHAMBER	1	8,500 GALLON REFRACTORY LINED MILD STEEL	10,000	COST CURVES	
T-3	MOLTEN SULFUR STORAGE TANK	1	1,700,000 GALLON, CARBON STEEL	120,000	COST CURVES	—
PUMPS						
P-1	SULFUR FEED PUMP (incl. motor)	2	100 GPM, CARBON STEEL, SS IMPELLER, SHAFT	4,000	TABER PUMP CO., INC.	NEG.
P-2	SULFUR PRODUCT PUMP (")	2	100 GPM, " " " " "	4,000	TABER PUMP CO., INC.	NEG.
P-3	SULFUR KNOCKOUT PUMP (")	2	10 GPM, " " " " "	3,000	TABER PUMP CO., INC.	NEG.
P-4	SULFUR SCRUBBER PUMPS (")	5	2000 GPM " " " " "	35,000	TABER PUMP CO., INC.	< 100 KWH/Hr
MISC.						
M-1	INERT GAS GENERATOR	1	100,000 CFH PACKAGED UNIT	35,000	C.M. KEMP MFG. CO., INC.	800 GPM C.W., 12 MM BTU/Hr, 25 KWH/Hr
M-2	SULFUR COOLER	1	100 MM BTU/Hr, 10,500 FT², CARBON STEEL	35,000	COST CURVES	6670 GPM C.W.
M-3	SULFUR SCRUBBER	1	18'D x 6' STAINLESS + MILD STEEL VESSEL PACKED WITH 2" RINGS	40,000	COST CURVES, U.S. STONEWARE	—

TOTAL COST MAJOR EQUIP. = $2,907,000

TABLE V-3

INVESTMENT COST DETERMINATION

1400 M.W. Power Plant	330 days @ 100% Capacity	0.3% SO_2 Flue Gas
Cost Element	**Factors**	**Costs**
Purchased Equipment	1.00	$2,907,000
Erection Labor	0.15	
Foundation & Platforms	0.07	
Piping	0.42	
Instruments	0.06	
Insulation	0.12	
Electrical	0.08	
Buildings	0.37	
Plant Facilities	0.15	
Plant Utilities, Land	0.24	
PHYSICAL PLANT COSTS	2.66	$7,800,000
Engineering & Construction	0.31	
DIRECT PLANT COST	2.97	$8,700,000
Contingency	0.26	
FIXED CAPITAL COSTS	3.22	$9,400,000
Interest During Construction	3%	300,000
Working Capital	6%	600,000
Initial Catalyst Charge	-	1,100,000
TOTAL INVESTMENT	$\sum$	$11,400,000

Generally Based on:

"New Cost Factors Give Quick, Accurate Estimates", C. A. Miller, Chemical Engineering, Sept. 13, 1965, p. 226 ff.

TABLE V-4

OPERATING COSTS

1400 M.W. Power Plant 330 days @ 100% Capacity (7920 Hrs.) 0.3% SO_2 Flue Gas

	Quantity	$/Hr.	$/Year
Raw Materials & Chemicals			
Catalyst Replacement-5 year life	1,750,000 lbs./yr.	$26/hr.	$210,000
Activated Alumina @ $.12/lb.			
Natural Gas (Methane for H_2S Generator)	included in utilities		
Treated Water for H_2S Generator	included in utilities		
Utilities			
Electricity @ 0.006/KW	7405 KWH/Hr.	45	356,000
Natural Gas @ $.50/mm BTU	341,000,000 BTU/hr.	171	1,350,000
Treated Water @ $.25/1000 gal.	33,600 gal./hr.	9	66,000
Cooling Water @ $.10/1000 gal.	450,000 gal./hr.	45	356,000
Labor			
*Direct @ $3.00/man hour	3 men/shift, round the clock 365 days	10	79,000
*Supervision $7800, $12000/yr.	4 supervisors, 1 superintendent	5	43,000
Payroll Burden @ 20%	% of direct labor, supervision	3	24,000
Operations			
*Maintenance + Supplies @ 5.75%**		68	540,000
Plant OVHD @ 50% of *		42	331,000
Capital Charges			
Depreciation @ 10%**		119	940,000
Taxes & Insurance @ 3%**		36	282,000
	Total Operating Costs	$579/hr.	$4,577,000 yr.

** Of Fixed Capital Costs

TABLE V-5

PRELIMINARY INVESTMENT & OPERATING COST FOR THE PCR CATALYTIC REDUCTION PROCESS - POWER PLANT APPLICATION CONCEPTUAL DESIGNS

Case Number	1	2	3	4	5
Process Description	Fig. V-2	Fig. V-3	Fig. V-4	Fig. V-5	Fig. V-6
TOTAL INVESTMENT, DOLLARS	3,558,000	5,415,000	11,452,000	7,450,000	10,703,000
ANNUAL OPERATING COST					
Gross Operating Cost,* $/Yr.	1,353,000	2,166,000	3,260,000	2,787,000	3,605,000
Coal Usage, Short Ton Coal/Yr.	2,217,000	2,217,000	2,217,000	2,217,000	2,217,000
Gross Operating Cost, $/Short Ton of Coal	0.61	0.98	1.47	1.26	1.63
Sulfur Produced, Short Ton/Yr.	38,000	61,100	44,700	61,100	61,100
By-product Sulfur Credit**, $/Yr.	1,425,000	2,295,000	1,677,000	2,291,000	2,291,000
Net Operating Cost, $/Yr.	72,000(cr)	125,000(cr)	1,584,000	496,000	1,314,000
Net Operating Cost, $/Short Ton of Coal	0.03(cr)	0.06(cr)	0.71	0.22	0.59

* Assumes capital dependent costs at 14% of investment.

** @ Price for bright sulfur of $37.50/short ton ($42.00/long ton).

Basis: 800 Megawatt power plant burning coal containing 3% sulfur. Produces 87,300,000 SCFH of flue gas containing 0.2% SO_2.

TABLE V-6

PRELIMINARY CAPITAL REQUIREMENTS FOR THE PCR CATALYTIC REDUCTION PROCESS - POWER PLANT APPLICATION

CONCEPTUAL DESIGNS

Basis: Same as Table V-5

	Case 1	Case 2	Case 3	Case 4	Case 5
H_2S Generation Equipment	$1,186,800	$1,341,500	$ 6,943,200	$2,017,100	$ 1,340,000
SO_2 Removal Equipment	239,900	480,400	921,800	3,385,800	3,387,200
Sulfur Recovery	1,132,100	1,912,600	1,205,500	328,300	2,270,700
Plant Facilities	127,900	187,000	453,600	286,600	350,400
Plant Utilities	188,000	274,000	666,700	421,300	506,100
Total Construction	2,874,700	4,196,000	10,190,800	6,439,100	7,854,400
Initial Catalyst Requirements	426,000	836,000	431,000	428,000	2,108,000
Total Plant Cost (Insurance & Tax Bases)	3,300,700	5,032,000	10,621,800	6,867,100	9,962,400
Interest During Construction	82,500	125,800	265,500	171,700	249,000
Subtotal for Depreciation	3,383,200	5,157,800	10,887,300	7,038,800	10,211,400
Working Capital	174,800	257,100	564,700	411,200	491,600
Total Investment	$3,558,000	$5,414,900	$11,452,000	$7,450,000	$10,703,000

TABLE V-7

PRELIMINARY OPERATING COST FOR THE PCR CATALYTIC REDUCTION PROCESS-POWER PLANT APPLICATION

Basis: Same as Table V-5

CONCEPTUAL DESIGNS

	Case 1	Case 2	Case 3	Case 4	Case 5
Direct Cost:					
Raw Material & Utilities					
Natural Gas, \$0.30/M cu.ft.	\$ 206,000	\$ 252,000	\$ 522,000	\$ 252,000	\$ 252,000
Power, \$0.006/kw-hr.	10,500	71,000	99,400	12,800	78,000
Heat, \$0.50/MM BTU (600°F)	198,700	536,000	None	363,500	500,000
Water, \$0.10/M gal.	24,600	8,000	119,400	2,700	6,000
Catalyst, \$0.30/lb.	85,200	85,600	86,200	500,000	540,000
	\$ 525,000	\$ 952,600	\$ 827,000	\$1,131,000	\$1,376,000
Direct Labor:					
Operating Labor, \$2.75/man-hr.	48,200	72,300	72,300	72,300	72,300
Supervision, 15% of labor	7,200	10,800	10,800	10,800	10,800
	\$ 55,400	\$ 83,100	\$ 83,100	\$ 83,100	\$ 83,100
Plant Maintenance:					
Maintenance Labor (M.L.)	72,000	96,000	216,000	144,000	180,000
Supervision, 20% of M.L.	14,400	19,200	43,200	28,800	36,000
Material, 50% of M.L.	36,000	48,000	108,000	72,000	90,000
	122,400	163,200	367,200	244,800	306,000
Payroll Overhead, 18.5% of Payroll	26,400	36,700	63,300	47,100	55,300
Operating Supplies, 20% of Plant Maintenance	24,500	32,600	73,400	49,000	61,200
TOTAL DIRECT COST	\$ 753,700	\$1,268,200	\$1,414,000	\$1,555,000	\$1,881,600
Indirect Cost: (Administration & General Overhead, 50% labor, maintenance and supplies)	101,200	139,500	243,500	188,500	225,200
Total Capital Charges, 14% of total investment	498,100	758,300	1,603,300	1,043,000	1,498,400
GROSS OPERATING COST	\$1,353,000	\$2,166,000	\$3,260,000	\$2,786,500	\$3,605,200

TABLE V-8

PRELIMINARY INVESTMENT AND OPERATING COSTS FOR SO_2 REMOVAL PROCESSES-POWER PLANT APPLICATION CONCEPTUAL DESIGN FOR PCR PROCESS

BASIS: 800 megawatt power plant burning coal containing 3% sulfur.
Produces 87,300,000 SCFH of flue gas containing 0.2% SO_2.

Process Description	PCR Catalytic Reduction Process (Case 2)	Reinluft Process	Alkalized Alumina Process	Catalytic Oxidation Process
Total Investment, Dollars	5,415,000	14,217,000	8,510,000	16,999,000
Annual Operating Cost				
Gross Operating Cost*, \$/yr.	2,166,000	5,431,000	3,402,000	3,881,000
Coal Usage, short ton coal/yr.	2,217,000	2,217,000	2,217,000	2,217,000
Gross Operating Cost, \$/short ton of coal	0.98	2.45	1.54	1.75
Sulfur Produced, short ton/yr.	61,100	60,126	59,730	57,778 (as 70% H_2SO_4)
By-product sulfur credit** \$/yr.	2,295,000	2,254,700	2,239,900	2,166,700
Net Operating Cost, \$/yr.	125,000(cr.)	3,176,300	1,162,300	1,714,300
Net Operating Cost, (or credit), \$/short ton of coal	0.06(cr.)	1.43	0.52	0.77

* Assumes capital dependent costs at 14% of investment.

** @ Price for bright sulfur of \$37.50/short ton (\$42.00/long ton). 70% H_2SO_4 is made in the catalytic oxidation process and credit is taken @ \$8.57/ton (equal to sulfur value). At \$15.35/ton credit, this process becomes breakeven.

TABLE V-9

PRELIMINARY CAPITAL REQUIREMENTS FOR SO_2 REMOVAL PROCESSES-POWER PLANT APPLICATION

BASIS: Same as Table V-8

CONCEPTUAL DESIGN FOR PCR PROCESS

	PCR Catalytic Reduction Process (Case 2)	Reinluft Process	Alkalized Alumina Process	Catalytic Oxidation Process
H_2S Generation equipment	$1,341,500	-	-	-
Absorber-regenerator	-	$ 9,629,000	$4,171,500	-
SO_2 Removal equipment	480,400	-	-	$13,727,000
Sulfuric acid plant	-	1,600,000	-	-
Gas producer	-	-	645,000	-
Sulfur recovery	1,912,600	-	1,780,000	-
Plant facilities	187,000	561,500	329,800	686,400
Plant Utilities	274,000	825,400	484,800	1,009,000
Total Construction	4,196,000	12,616,200	7,411,100	15,423,000
Initial catalyst requirements	836,000	465,600	341,600	699,300
Total Plant Cost (insurance & tax bases)	5,032,000	13,081,000	7,752,700	16,122,300
Interest during construction	125,800	327,000	193,000	403,100
Subtotal for depreciation	5,157,800	13,408,800	7,946,500	16,525,400
Working capital	257,100	808,200	563,500	473,600
Total Investment	$5,414,900	$14,217,000	$8,510,000	$16,999,000

TABLE V-10

PRELIMINARY OPERATING COSTS FOR SO_2 REMOVAL PROCESSES-POWER PLANT APPLICATION

BASIS: Same as Table V-8

CONCEPTUAL DESIGN FOR
PCR PROCESS

	PCR Catalytic Reduction Process (Case 2)		Reinluft Process		Alkalized Alumina Process		Catalytic Oxidation Process	
Direct Cost:								
Raw Mat'l & Utilities								
Nat. gas, $0.30/M cu. ft.	252,000		-		-		-	
Char, $80/ton	-		2,122,200		-		-	
Coal, $4/ton	-		-		475,200		-	
Adsorbent makeup, $0.25/lb.	-		-		901,700		-	
Power, $0.006/kw.hr.	71,000		70,000		90,300		145,700	
Steam, $0.50/M lbs.	-		202,400(cr.)		-		18,200	
Heat, $0.50/MM Btu* (600°F)	536,000		211,200		124,400 (incl. cr.)		-	
Water, $0.10/M gal.	8,000		107,500		26,100		72,600	
Catalyst**	85,600		-		-		139,900	
		952,600		2,308,500		1,617,700		376,400
Direct Labor:								
Operating Labor, $2.75/ man-hr.	72,300		96,400		72,300		72,300	
Supervision, 15% of labor	10,800	83,100	14,500	110,900	10,800	83,100	10,800	83,100
Plant Maintenance:								
Maintenance Labor	96,000		288,000		138,000		300,000	
Supervision	19,200		57,000		27,600		60,000	
Material	48,000	163,200	144,000	498,600	69,000	234,600	150,000	510,000
Payroll Overhead, 18.5% of payroll		36,700		84,500		46,000		82,000
Operating Supplies, 20% of plant maint.		32,600		97,900		46,900		102,000
TOTAL DIRECT COST		1,268,200		3,091,400		2,028,300		1,153,500

* Except for alkalized alumina process where part of heat used for regeneration (1200°F) is charged at $0.70/MM Btu.

** Catalyst cost: $1.40/liter for catalytic oxidation process; $0.30/lb. for PCR catalytic reduction process (5 year life for both processes assumed).

TABLE V-10 (cont.)

PRELIMINARY OPERATING COSTS FOR SO_2 REMOVAL PROCESSES

POWER PLANT APPLICATION

CONCEPTUAL DESIGN FOR PCR PROCESS

	Annual Operating Cost, Dollars			
	PCR Catalytic Reduction Process	Reinluft Process	Alkalized Alumina Process	Catalytic Oxidation Process
Indirect Cost: (administration & general overhead, 50% labor, maintenance & supplies)	139,500	349,200	182,300	347,600
Total capital charges, 14% of total investment	758,300	1,990,400	1,191,400	2,379,900
GROSS OPERATING COST	2,166,000	5,431,000	3,402,000	3,881,000

TABLE V-11

PRELIMINARY INVESTMENT AND OPERATING COSTS FOR PCR CATALYTIC REDUCTION PROCESS - COPPER ORE SMELTING

CONCEPTUAL DESIGN

BASIS: Smelting unit processes 1630 short tons/day of ore. Produces 70,000,000 SCF/day of flue gas containing 2% SO_2.

Process Description	PCR Catalytic Reduction Process Case 1	 Case 2
Total Investment, Dollars	1,184,200	1,753,400
Gross Annual Operating Cost*, $/Yr.	469,000	717,100
By-Product Credit		
Sulfur produced, short tons/yr.	19,200	20,200
Annual sales value of sulfur, $/yr. (@ $37.50/short ton)	720,400	756,000
Profit		
Net annual operating credit, $/yr.	251,400	38,900
Return on investment (before taxes), %	21.2	2.2

* Assumes capital dependent costs at 10% of investment.

TABLE V-12

PRELIMINARY TOTAL CAPITAL REQUIREMENTS FOR THE PCR CATALYTIC REDUCTION PROCESS - COPPER ORE SMELTING CONCEPTUAL DESIGN

BASIS: Same as Table V-11

Process Description	Capital Cost Case 1	Capital Cost Case 2
H_2S Generation Equipment	\$604,600	\$518,500
SO_2 Removal Equipment	31,600	110,500
Sulfur Recovery	304,200	668,900
Plant Facilities	47,000	64,800
Plant Utilities	69,100	95,400
Total Construction	1,056,500	1,458,100
Initial Catalyst Requirements	27,500	138,300
Total Plant Cost (Insurance & Tax Bases)	1,084,000	1,596,400
Interest During Construction	27,100	39,900
Subtotal for Depreciation	1,111,100	1,636,300
Working Capital	73,100	117,100
TOTAL INVESTMENT	\$1,184,200	\$1,753,400

TABLE V-13
PRELIMINARY OPERATING COST
FOR THE PCR CATALYTIC REDUCTION PROCESS - COPPER ORE SMELTING
CONCEPTUAL DESIGN

BASIS: Same as Table V-11

	Annual Operating Cost			
Process Description	Case 1		Case 2	
Direct Cost:				
Raw Materials & Utilities				
Natural Gas @ $0.30/M cu.ft.	$78,400		$ 82,000	
Power @ $0.006/kw. hr.	5,300		25,900	
Heat @ $0.50/MM Btu	75,200		124,000	
Water @ $0.10/M gal.	1,200		2,700	
Catalyst @ $0.30/lb.	18,300		27,700	
		$178,400		$262,300
Direct Labor				
Operating Labor, $2.75/man-hr.	48,200		72,300	
Supervision, 15% of O.L.	7,200		10,800	
		55,400		83,100
Plant Maintenance				
Maint. Labor, $6,000/man yr.	24,000		48,000	
Supervision, 20% of M.L.	4,800		9,600	
Material, 50% of M.L.	12,000		24,000	
		40,800		71,600
Payroll Overhead, 18.5% of Payroll		15,600		26,000
Operating Supplies, 20% of Plant Maintenance		8,200		14,300
TOTAL DIRECT COST		298,400		457,300
Indirect Cost:				
(Administration & General Overhead), 50% of Labor, Maint. & Supplies		52,200		84,500
Total Capital Charges, 10% of Total Investment		118,400		175,300
GROSS OPERATING COST		$469,000		$717,100

TABLE V-14

BASES USED IN PRELIMINARY ECONOMIC EVALUATION - CONCEPTUAL DESIGNS

The following general assumptions presented by Katell were paralleled in this analysis:

Power Plant:

1. Coal analysis, percent:

Carbon	70.1
Oxygen	6.6
Hydrogen	4.9
Nitrogen	1.4
Sulfur	3.0
Ash	12.7
Moisture	1.3

2. Coal combustion:
    Excess air: 20%
    Coal burned per hour: 280 ton
    Heating value: 12,800 Btu/lb.

3. Flue gas from 800-MW power plant: 87.3 million std. cu. ft./hr. (contains 0.2% SO_2)

4. Sulfur in coal:
    Burns to SO_3: 2%
    Burns to SO_2: 98%

5. Ash content of flue gas as fed to SO_2 removal units: Essentially zero

Copper Smelter:

1. Flue gas from 1630 tons of ore/day plant: 70 million std. cu. ft./day (contains 2.0% SO_2)

2. Ash content of flue gas as fed to SO_2 removal units: Essentially zero

TABLE V-14 (cont.)

PCR Process(all cases) :

1. H_2S Generator: Space velocity, 400 vol./vol./hr. (9 second contact time); activated alumina catalyst, 8-9 mesh; density, 54 lbs./cu. ft.
2. SO_2 Reactor: Space velocity, 2800 vol./vol./hr. (2 second contact time); alumina catalyst (Spence), 10-20 mesh; density, 44 lbs./cu. ft.
3. Catalyst cost: $0.30/lb. (both reactors)
4. Catalyst life: 5 years (both reactors)

TABLE V-14 (cont.)

INVESTMENT

Basic Equipment Cost - Basic equipment cost data was obtained from the following sources:

1. Costs of Process Equipment, Reprinted from Chemical Engineering, March 16, 1964.
2. Chemical Engineering Costs, Dryden, C. E., Winfield, M. D., Special Report #29, Engineering Experiment Station, Ohio State University, 1963.
3. Quotations from equipment vendors (sulfur scrubbers and inert gas generator).

An allowance of 10% was added to the cost of major equipment to allow for unlisted items.

Total Construction Cost

Item	Basis for Costing
Basic Equipment	Individually sized and costed
Installed Cost*	Basic equipment cost + 130% of Basic Equipment cost
Field Overhead & Profit	6.9% of Installed Cost
Engineering	15% of Basic Equipment Cost
Subtotal	Summation of the above 4 items
Contingency	10% of the Subtotal
Total Battery Limits	Summation of Subtotal with Contingency
Plant Facilities	5% of Battery Limits
Plant Utilities	7% of Battery Limits & Plant Facilities
Total Construction Cost	Summation of Battery Limits, Plant Facilities & Plant Utilities

* Method reported by Miller, C.A., Chem. Engrg., pg. 226, Sept. 13, 1965. Includes basic equipment, field erection, equipment foundations and structural supports, piping, insulation, electrical, instrumentation, site preparation, painting, buildings and structural and building services.

Total Capital Cost - Total construction cost plus initial catalyst requirement, interest during construction and working capital.

Initial Catalyst Requirement

$$\text{Lbs. Catalyst} = \frac{\text{gas rate, cu. ft./hr}}{\text{space vel., } \frac{\text{cu. ft./hr.}}{\text{cu. ft. cat.}}} \times \text{Cat. density, lbs./cu.ft.cat.}$$

Interest during construction - Taken as 2.5% of total plant cost (total construction cost + initial catalyst requirement).

Working Capital

Catalyst, 60 day's supply - assumes 5 yr. catalyst life
Direct labor (operating & maintenance), 3 months
Payroll overhead, 3 months
Operating supplies, 3 months
Indirect cost, 4 months
Fixed cost, 0.5% of total construction cost plus initial catalyst requirement
Spare parts, 1% of total construction cost
Miscellaneous expense, 1.1% of total construction cost.

OPERATING COST

Utilities and Catalyst Requirements - Heat, power and water requirements were calculated from the temperatures and quantities of materials shown on the process flow sheets. Natural gas was used to supply thermal energy as well as raw material fed to the H_2S generation step. Catalyst requirement was calculated from quantities of reactant gas shown on the process flow diagrams and the space velocities and apparent bulk densities assumed. Physical constants were obtained from:

1. Tuller, W. N., The Sulfur Data Book, (Freeport Sulfur Co.), McGraw Hill, 1954.
2. Perry, J. H. (Editor), Chemical Engineering Handbook, Third Edition, McGraw Hill, 1950.
3. McAdams, W. H., Heat Transmission, McGraw Hill, 1954.

TABLE IV-14 (cont.)

Development of Operating Costs

Direct materials - charged as follows:

- Natural gas, $0.30 per thousand cubic feet
- Power, $0.006 per kilowatt hour
- Heat (assuming 60% thermal efficiency), $0.50 per thousand cubic feet
- Water, $0.10 per thousand gallons
- Catalyst, $0.30 per pound
- Operating labor, $2.75 per man-hour
- Operating supervision, 15% of operating labor
- Maintenance labor*, $6,000 per man-year
- Maintenance supervision*, 20% of maintenance labor
- Maintenance materials*, 50% of maintenance labor
- Payroll overhead, 18% of payroll
- Operating supplies, 20% of all maintenance costs
- Indirect charges (administration & general overhead), 50% of labor, maintenance and supplies
- Capital charges**, 14% of total investment for power plant applications
  - 10% of total investment for copper smelter applications

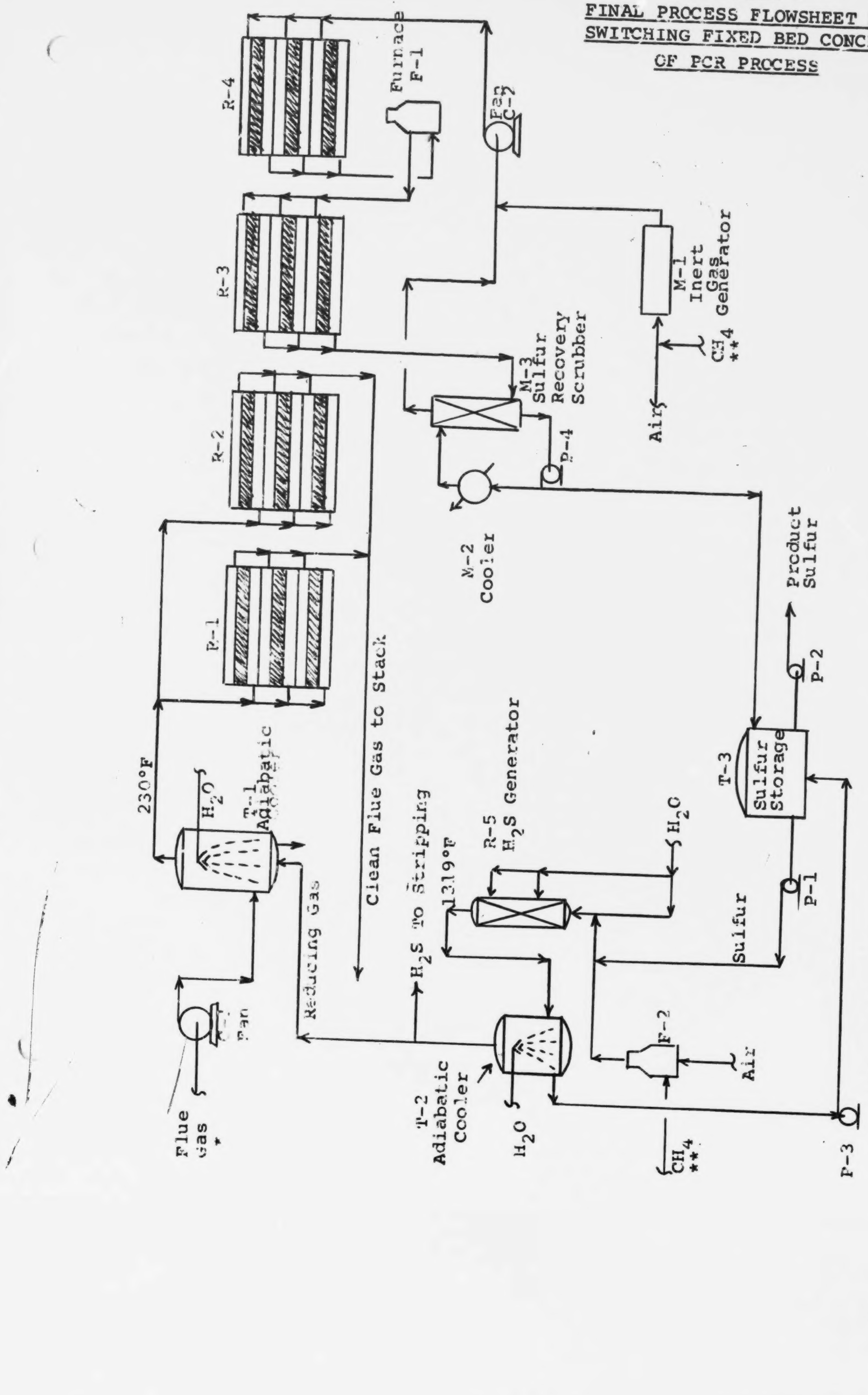
---

* Annual maintenance (labor, supervision and materials) was taken equal to 3.9% of total construction cost.

** Includes depreciation, taxes and insurance.

FIGURE V-1

FINAL PROCESS FLOWSHEET FOR SWITCHING FIXED BED CONCEPT OF PCR PROCESS


R-4
Furnace F-1
Fan C-2
R-3
R-2
R-1
M-1 Inert Gas Generator
CH4 **
Air
M-3 Sulfur Recovery Scrubber
P-4
M-2 Cooler
Product Sulfur
P-2
Clean Flue Gas to Stack
230°F
H2O
T-1 Adiabatic Cooler
Reducing Gas
Fan
Flue Gas *
H2S To Stripping
1319°F
R-5 H2S Generator
H2O
T-3 Sulfur Storage
P-1
Sulfur
F-2
Air
T-2 Adiabatic Cooler
H2O
CH4 **
P-3

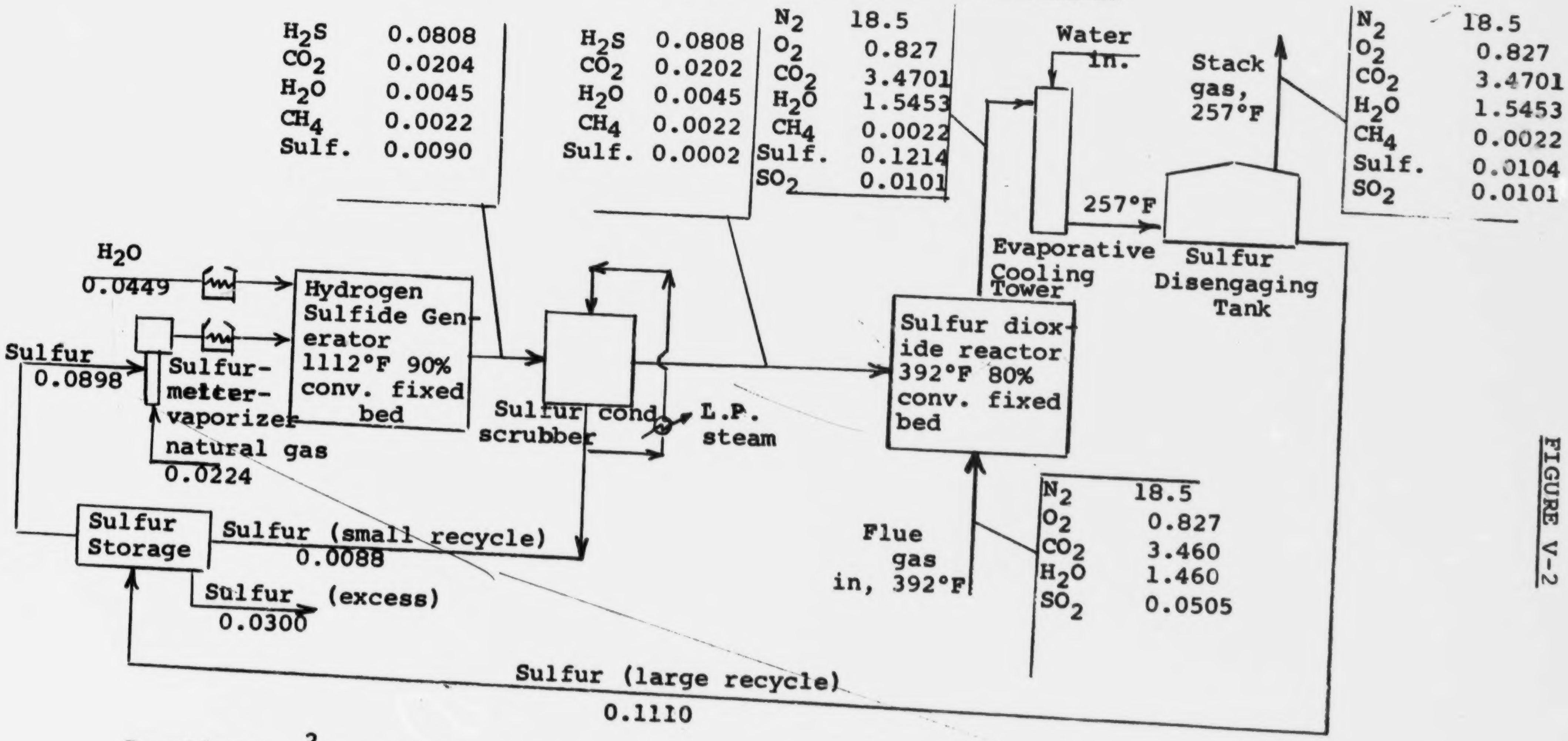
R-1, R-2 Reactors Reducing
R-3, Reactors Regenerating
R-4, Reactors Cooling

* From Electrostatic Precipitator; 300°F, -19'H_2O
** Natural Gas From Pipeline

FIGURE V-2

PCR PROCESS, CASE 1. CATALYTIC REDUCTION OF SO_2 IN FLUE GAS WITH H_2S : (POWER PLANT)

FIXED BED REACTORS - STEADY-STATE OPERATION


H2S 0.0808
CO2 0.0204
H2O 0.0045
CH4 0.0022
Sulf. 0.0090
H2S 0.0808
CO2 0.0202
H2O 0.0045
CH4 0.0022
Sulf. 0.0002
N2 18.5
O2 0.827
CO2 3.4701
H2O 1.5453
CH4 0.0022
Sulf. 0.1214
SO2 0.0101
Water in.
Stack gas, 257°F
N2 18.5
O2 0.827
CO2 3.4701
H2O 1.5453
CH4 0.0022
Sulf. 0.0104
SO2 0.0101
257°F
H2O
0.0449
Hydrogen Sulfide Generator 1112°F 90% conv. fixed bed
Evaporative Cooling Tower
Sulfur Disengaging Tank
Sulfur
0.0898
Sulfur-melter-vaporizer
natural gas
0.0224
Sulfur cond scrubber
L.P. steam
Sulfur dioxide reactor 392°F 80% conv. fixed bed
N2 18.5
O2 0.827
CO2 3.460
H2O 1.460
SO2 0.0505
Flue gas in, 392°F
Sulfur Storage
Sulfur (small recycle)
0.0088
Sulfur (excess)
0.0300
Sulfur (large recycle)
0.1110

Reactions: $\frac{2}{X} S_X + \frac{1}{2} CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2} CO_2$

$SO_2 + 2H_2S \longrightarrow \frac{3}{X} S_X + 2H_2O$

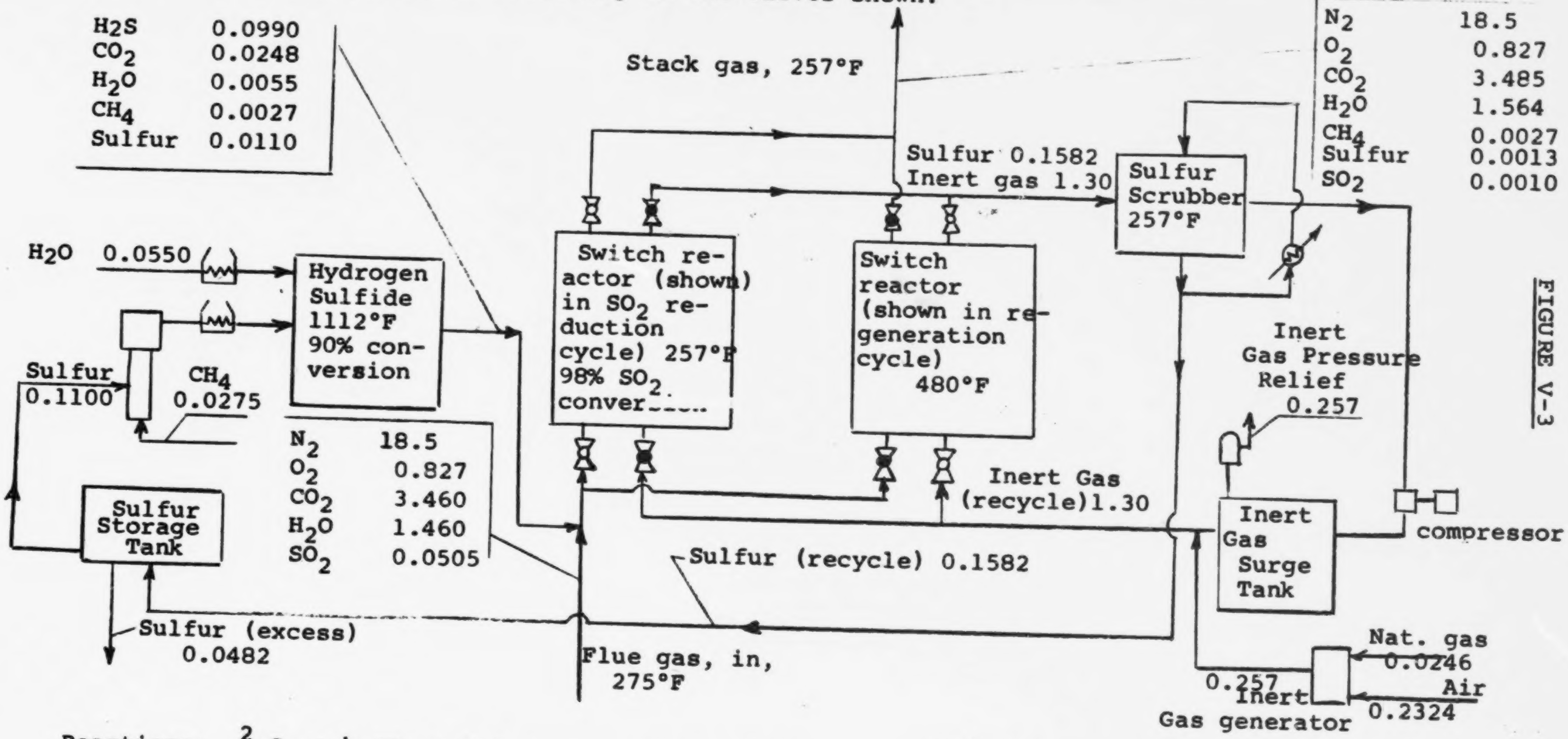
Notes: Basis: 800 megawatt power plant burning coal containing 3% sulfur.
All numbers represent lb-moles/hr. x 10^{-4}.
Sulfur is expressed as lb-atoms/hr. x 10^{-4}.

CONCEPTUAL DESIGN

FIGURE V-3

PCR PROCESS, CASE 2. CATALYTIC REDUCTION OF SO_2 IN POWER PLANT FLUE GAS WITH H_2S: SO_2 REACTORS: FIXED BED - NON-STEADY-STATE OPERATION

Two identical switch reactors are operated alternately on SO_2 reduction and sulfur stripping cycles by a time-scheduled reversing of the valves shown.


H2S 0.0990
CO2 0.0248
H2O 0.0055
CH4 0.0027
Sulfur 0.0110
Stack gas, 257°F
N2 18.5
O2 0.827
CO2 3.485
H2O 1.564
CH4 0.0027
Sulfur 0.0013
SO2 0.0010
Sulfur 0.1582
Inert gas 1.30
Sulfur Scrubber 257°F
H2O 0.0550
Hydrogen Sulfide 1112°F 90% conversion
Switch reactor (shown in SO2 reduction cycle) 257°F 98% SO2 conversion
Switch reactor (shown in regeneration cycle) 480°F
Inert Gas Pressure Relief 0.257
Sulfur 0.1100
CH4 0.0275
N2 18.5
O2 0.827
CO2 3.460
H2O 1.460
SO2 0.0505
Inert Gas (recycle) 1.30
Sulfur Storage Tank
Sulfur (recycle) 0.1582
Inert Gas Surge Tank
compressor
Sulfur (excess) 0.0482
Flue gas, in, 275°F
Nat. gas 0.0246
Air 0.2324
0.257
Inert Gas generator
FIGURE V-3

Reactions: $\frac{2}{X} S_X + \frac{1}{2} CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2} CO_2$ $\qquad SO_2 + H_2S \longrightarrow \frac{3}{X} S_X + 2H_2O$

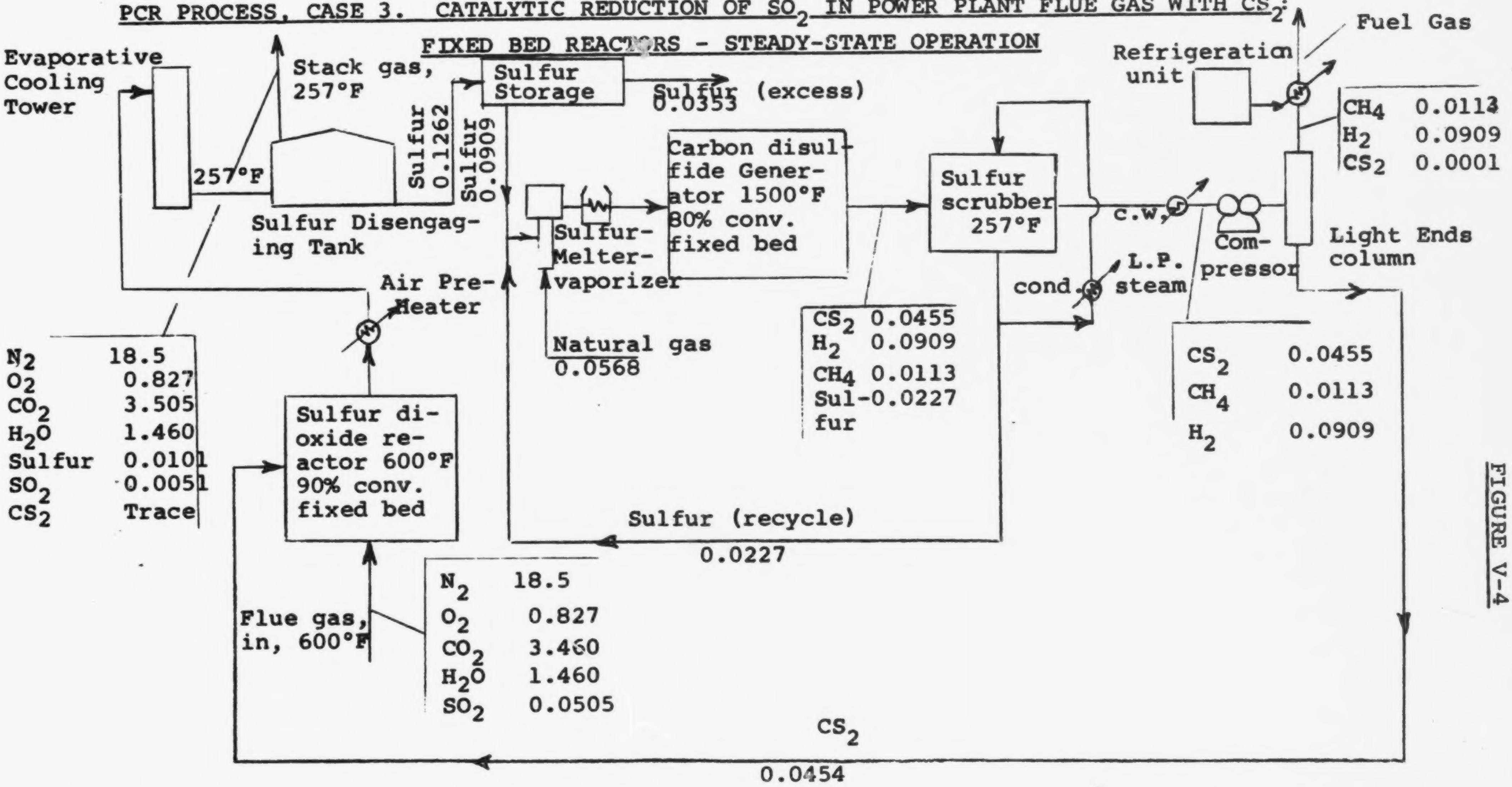
Notes: Basis: 800 megawatt power plant burning coal containing 3% sulfur.
All numbers represent lb-moles/hr. x 10^{-4}.
Sulfur is expressed in lb-atoms/hr. x 10^{-4}.

CONCEPTUAL DESIGN

FIGURE V-4

PCR PROCESS, CASE 3. CATALYTIC REDUCTION OF SO_2 IN POWER PLANT FLUE GAS WITH CS_2:

FIXED BED REACTORS - STEADY-STATE OPERATION


Evaporative Cooling Tower
Stack gas, 257°F
257°F
Sulfur Disengaging Tank
Sulfur 0.1262
Sulfur 0.0909
Sulfur Storage
Sulfur (excess) 0.0353
Sulfur-Melter-vaporizer
Natural gas 0.0568
Carbon disulfide Generator 1500°F 80% conv. fixed bed
Sulfur scrubber 257°F
c.w.
cond.
L.P. steam
Compressor
Refrigeration unit
Fuel Gas
Light Ends column
CH4 0.0113
H2 0.0909
CS2 0.0001
CS2 0.0455
CH4 0.0113
H2 0.0909
CS2 0.0455
H2 0.0909
CH4 0.0113
Sulfur 0.0227
Air Pre-Heater
N2 18.5
O2 0.827
CO2 3.505
H2O 1.460
Sulfur 0.0101
SO2 0.0051
CS2 Trace
Sulfur dioxide reactor 600°F 90% conv. fixed bed
Flue gas, in, 600°F
N2 18.5
O2 0.827
CO2 3.460
H2O 1.460
SO2 0.0505
Sulfur (recycle) 0.0227
CS2 0.0454

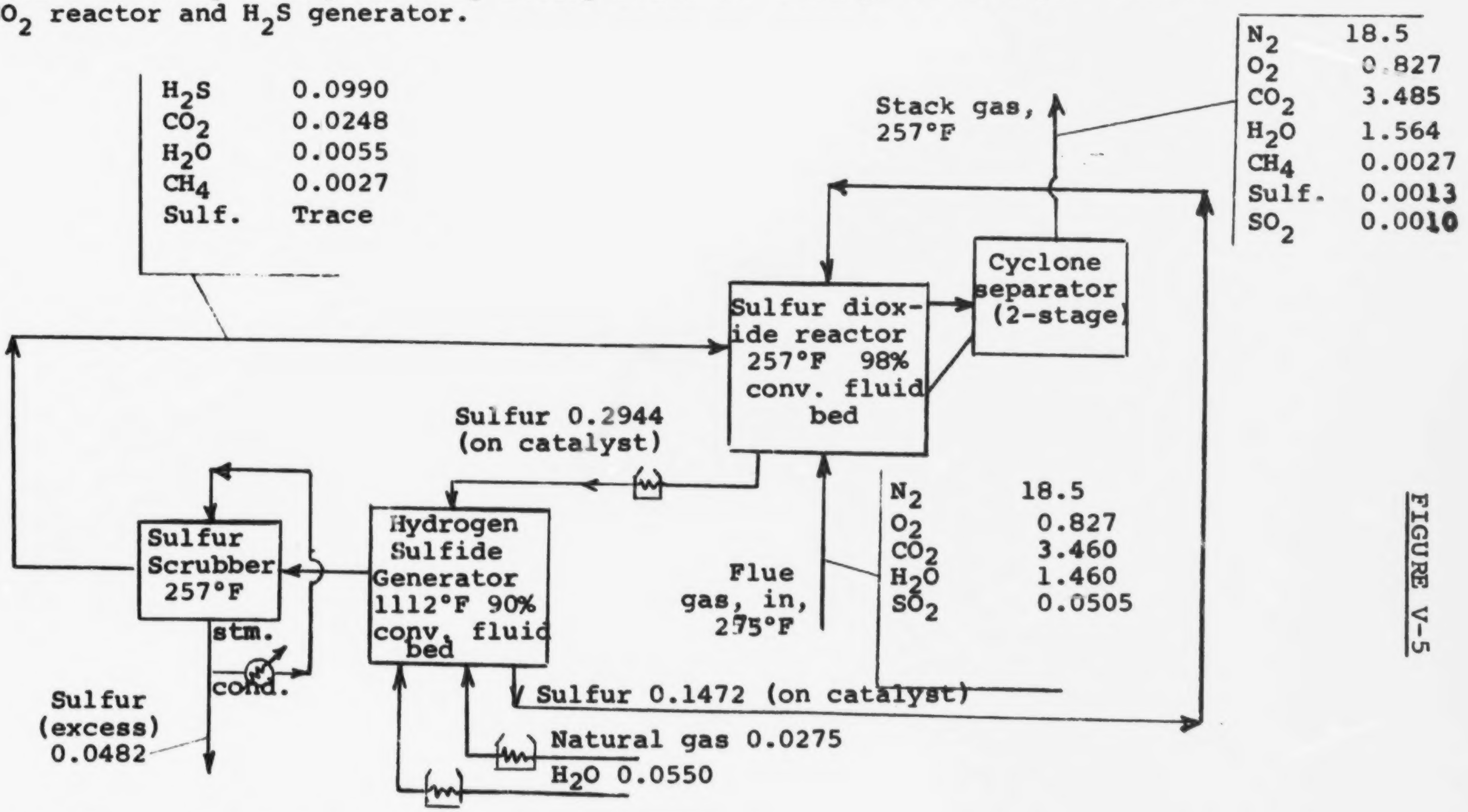
Reaction: $\frac{2}{X} S_X + CH_4 \longrightarrow CS_2 + 2H_2$ $SO_2 + CS_2 \longrightarrow \frac{3}{X} S_X + CO_2$

Notes: Basis: 800 megawatt power plant burning coal containing 3% sulfur.
All numbers represent lb-moles/hr. x 10^{-4}.
Sulfur is expressed as lb-atoms/hr. x 10^{-4}.

CONCEPTUAL DESIGN

FIGURE V-5
PCR PROCESS, CASE 4. CATALYTIC REDUCTION OF SO_2 IN POWER PLANT FLUE GAS WITH H_2S: FLUID BED REACTORS

Sulfur recovery accomplished by steady-state interchange of catalyst between SO_2 reactor and H_2S generator.


H2S 0.0990
CO2 0.0248
H2O 0.0055
CH4 0.0027
Sulf. Trace
Stack gas, 257°F
N2 18.5
O2 0.827
CO2 3.485
H2O 1.564
CH4 0.0027
Sulf. 0.0013
SO2 0.0010
Cyclone separator (2-stage)
Sulfur dioxide reactor 257°F 98% conv. fluid bed
Sulfur 0.2944 (on catalyst)
N2 18.5
O2 0.827
CO2 3.460
H2O 1.460
SO2 0.0505
Flue gas, in, 275°F
Sulfur Scrubber 257°F
Hydrogen Sulfide Generator 1112°F 90% conv. fluid bed
stm.
cond.
Sulfur (excess) 0.0482
Sulfur 0.1472 (on catalyst)
Natural gas 0.0275
H2O 0.0550

Reactions: $\frac{2}{X} S_X + \frac{1}{2} CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2} CO_2$

$SO_2 + 2H_2S \longrightarrow \frac{3}{X} S_X + 2H_2O$

Notes: Basis: 800 megawatt power plant burning coal containing 3% sulfur.
All numbers represent lb-moles/hr. x 10^{-4}.
Sulfur is expressed in lb-atoms/hr. x 10^{-4}.

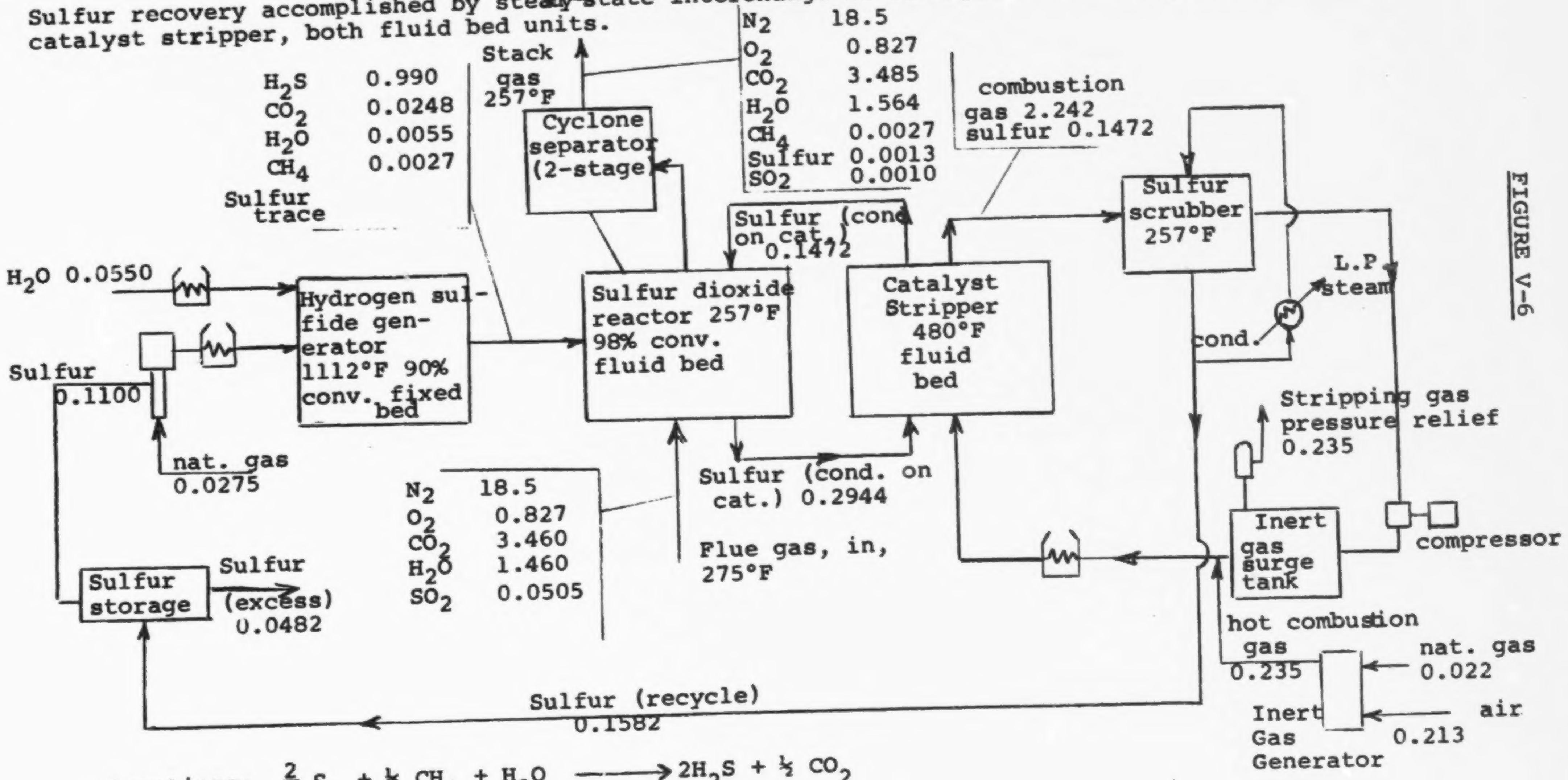
CONCEPTUAL DESIGN

FIGURE V-5

FIGURE V-6

PCR PROCESS, CASE 5. CATALYTIC REDUCTION OF SO_2 IN POWER PLANT FLUE GAS WITH H_2S: SO_2 REACTOR & STRIPPER: FLUID BED - H_2S GENERATOR: FIXED BED - STEADY-STATE

Sulfur recovery accomplished by steady-state interchange of catalyst between SO_2 reactor and catalyst stripper, both fluid bed units.


Stack gas 257°F
H_2S 0.990
CO_2 0.0248
H_2O 0.0055
CH_4 0.0027
Sulfur trace
N_2 18.5
O_2 0.827
CO_2 3.485
H_2O 1.564
CH_4 0.0027
Sulfur 0.0013
SO_2 0.0010
combustion gas 2.242
sulfur 0.1472
Cyclone separator (2-stage)
Sulfur (cond on cat.) 0.1472
Sulfur scrubber 257°F
H_2O 0.0550
Hydrogen sulfide generator 1112°F 90% conv. fixed bed
Sulfur dioxide reactor 257°F 98% conv. fluid bed
Catalyst Stripper 480°F fluid bed
L.P. steam
cond.
Sulfur 0.1100
nat. gas 0.0275
Stripping gas pressure relief 0.235
Sulfur (cond. on cat.) 0.2944
N_2 18.5
O_2 0.827
CO_2 3.460
H_2O 1.460
SO_2 0.0505
Flue gas, in, 275°F
Inert gas surge tank
compressor
Sulfur storage
Sulfur (excess) 0.0482
hot combustion gas 0.235
nat. gas 0.022
air 0.213
Inert Gas Generator
Sulfur (recycle) 0.1582

Reactions: $\frac{2}{x} S_x + \frac{1}{2} CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2} CO_2$

$SO_2 + 2H_2S \longrightarrow \frac{3}{x} S_x + 2H_2O$

Notes: Basis: 800 megawatt power plant burning coal containing 3% sulfur.
All numbers represent lb-moles/hr. x 10^{-4}.
Sulfur is expressed as lb-atoms/hr. x 10^{-4}.

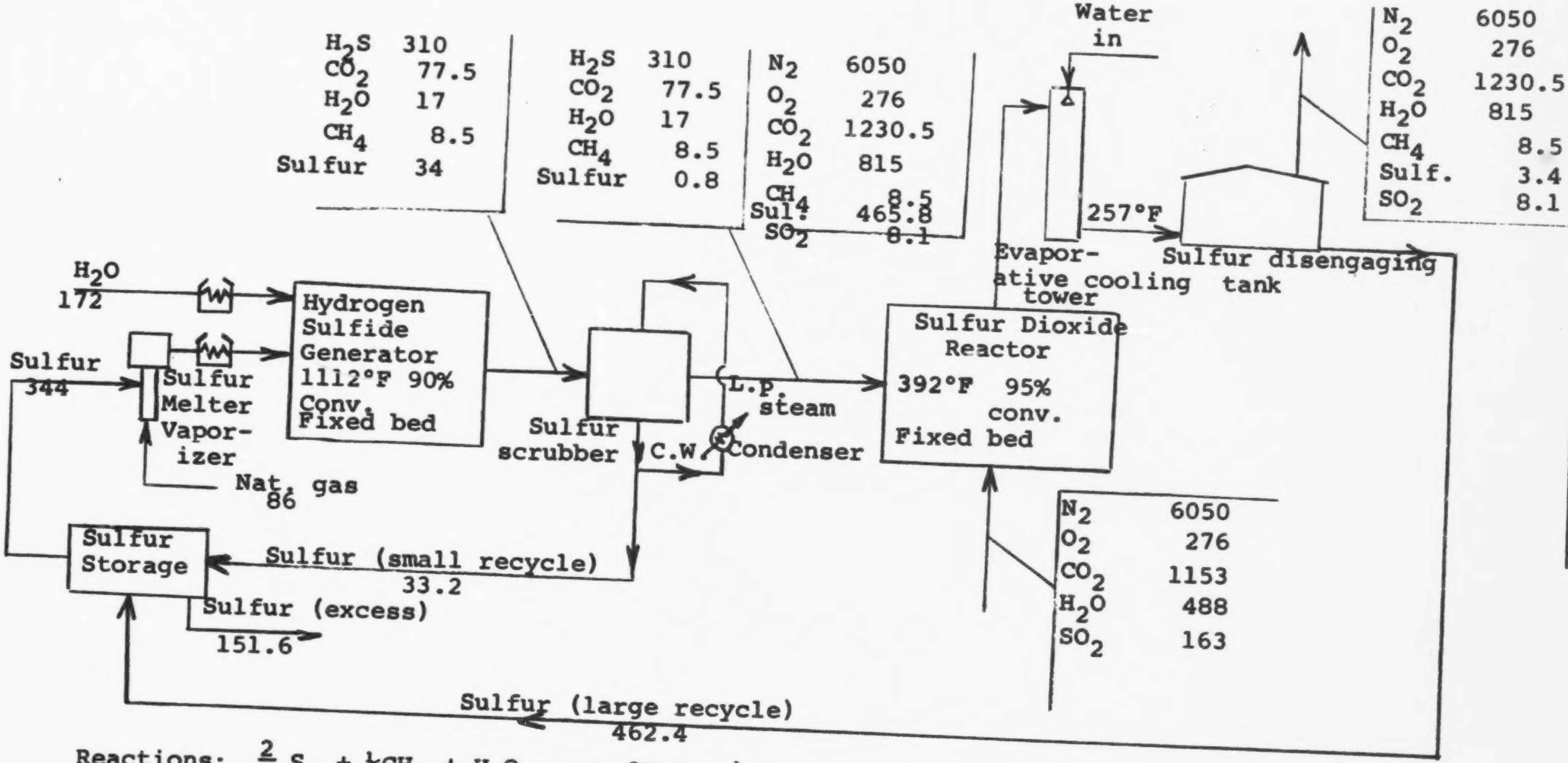
CONCEPTUAL DESIGN

FIGURE V-6

FIGURE V-7

PCR PROCESS, CASE 1. CATALYTIC REDUCTION OF SO_2 IN FLUE GAS FROM COPPER ORE SMELTING PLANT

FIXED BED REACTORS - STEADY-STATE OPERATION


H_2S 310
CO_2 77.5
H_2O 17
CH_4 8.5
Sulfur 34
H_2S 310
CO_2 77.5
H_2O 17
CH_4 8.5
Sulfur 0.8
N_2 6050
O_2 276
CO_2 1230.5
H_2O 815
CH_4 8.5
Sul. 465.8
SO_2 8.1
Water in
N_2 6050
O_2 276
CO_2 1230.5
H_2O 815
CH_4 8.5
Sulf. 3.4
SO_2 8.1
257°F
Evaporative cooling tower
Sulfur disengaging tank
H_2O 172
Sulfur 344
Sulfur Melter Vaporizer
Nat. gas 86
Hydrogen Sulfide Generator 1112°F 90% Conv. Fixed bed
Sulfur scrubber
C.W.
L.P. steam
Condenser
Sulfur Dioxide Reactor 392°F 95% conv. Fixed bed
N_2 6050
O_2 276
CO_2 1153
H_2O 488
SO_2 163
Sulfur Storage
Sulfur (small recycle) 33.2
Sulfur (excess) 151.6
Sulfur (large recycle) 462.4

Reactions: $\frac{2}{X} S_X + \frac{1}{2}CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2}CO_2$

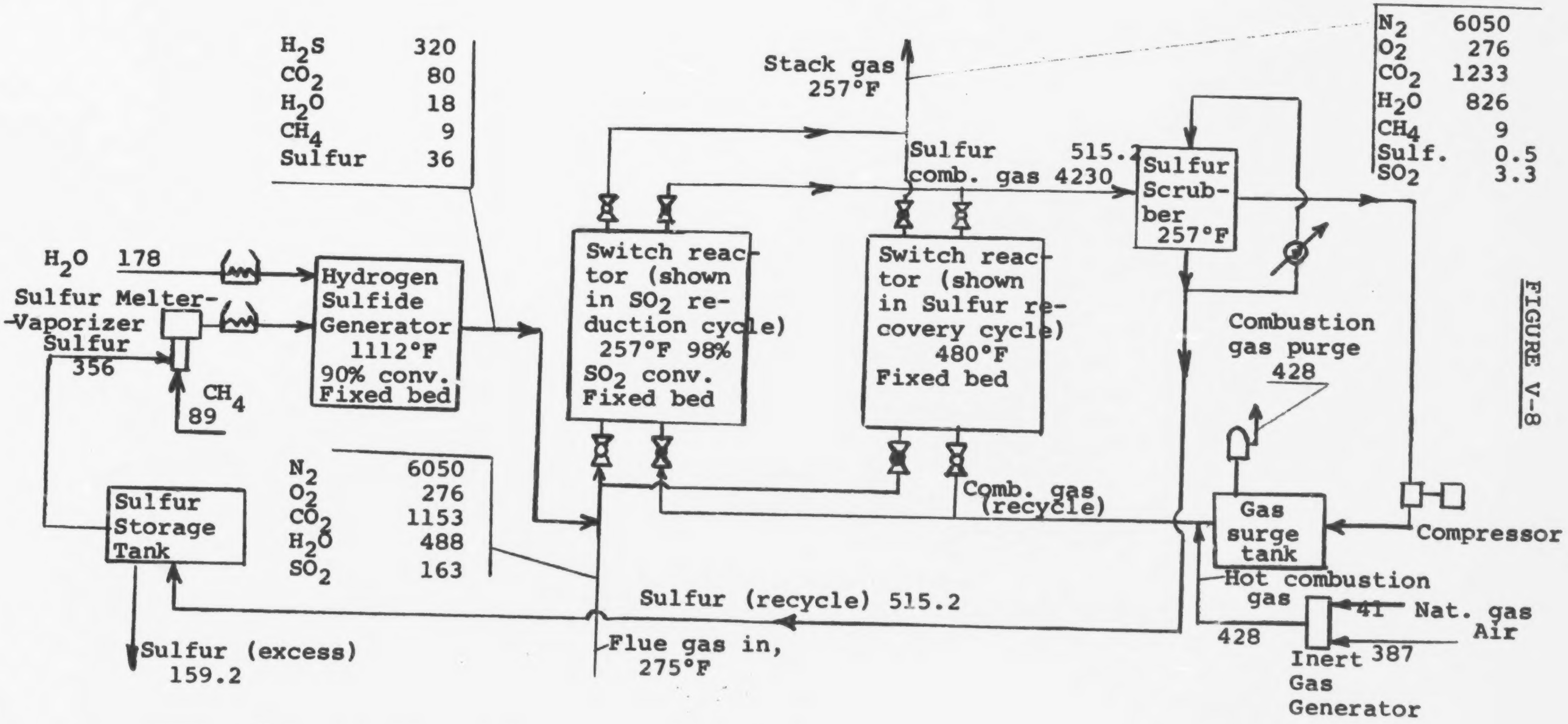
$SO_2 + 2H_2S \longrightarrow \frac{3}{X} S_X + 2H_2O$

Basis: 1630 ton/day copper ore smelter.
Rates given are in lb-moles/hr.; sulfur is expressed in lb-atoms/hr.

CONCEPTUAL DESIGN

FIGURE V-7

FIGURE V-8
PCR PROCESS, CASE 2. CATALYTIC REDUCTION OF SO_2 IN FLUE GAS FROM COPPER ORE SMELTING PLANT
SO_2 REACTORS: FIXED BED - NON-STEADY-STATE H_2S GENERATOR: FIXED BED - STEADY-STATE


H_2S 320
CO_2 80
H_2O 18
CH_4 9
Sulfur 36
Stack gas
257°F
N_2 6050
O_2 276
CO_2 1233
H_2O 826
CH_4 9
Sulf. 0.5
SO_2 3.3
Sulfur 515.2
comb. gas 4230
Sulfur Scrub-ber 257°F
H_2O 178
Sulfur Melter-Vaporizer
Sulfur 356
CH_4 89
Hydrogen Sulfide Generator 1112°F 90% conv. Fixed bed
Switch reactor (shown in SO_2 reduction cycle) 257°F 98% SO_2 conv. Fixed bed
Switch reactor (shown in Sulfur recovery cycle) 480°F Fixed bed
Combustion gas purge 428
FIGURE V-8
N_2 6050
O_2 276
CO_2 1153
H_2O 488
SO_2 163
Sulfur Storage Tank
Comb. gas (recycle)
Gas surge tank
Compressor
Hot combustion gas
41 Nat. gas
Air
428
387
Inert Gas Generator
Sulfur (recycle) 515.2
Sulfur (excess) 159.2
Flue gas in, 275°F

Reactions: $\frac{2}{X} S_X + \frac{1}{2} CH_4 + H_2O \longrightarrow 2H_2S + \frac{1}{2}CO_2$

$SO_2 + 2H_2S \longrightarrow \frac{3}{X} S_X + 2H_2O$

Basis: 1630 ton/day copper ore smelter.
Rates given are in lb-moles/hr.; sulfur is expressed in lb-atoms/hr.

CONCEPTUAL DESIGN

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION VI

LITERATURE REVIEW

TABLE OF CONTENTS

SECTION VI - LITERATURE REVIEW

Page

1. Reaction of Hydrogen Sulfide and Sulfur Dioxide 207
   1.1 Commercial Processes for H_2S Recovery 207
   1.2 Application to Low SO_2 Concentrations 208
   1.3 Catalysts 208
   1.4 H_2S in the Effluent 210
   1.5 Thermodynamics 210
   1.6 Reaction of H_2S and SO_2 in Solution 210
2. Methane-Sulfur Reaction 211
   2.1 Reactant Purity 211
   2.2 Commercial Processes 212
   2.3 Catalysts 212
   2.4 Reaction Conditions 213
   2.5 Liquid Phase 213
   2.6 Production of CS_2 Without H_2S 214
   2.7 Use of Hydrocarbons Other Than CH_4 216
   2.8 H_2S From SO_2 + CH_4 216
   2.9 Adsorbents Containing Sulfur Treated with Methane to Recover H_2S 216
   2.10 Kinetic Studies 217
3. List of References 220

LIST OF TABLES

SECTION VI - LITERATURE REVIEW

Table	Title	Page
VI-1	Reduction of SO_2 With H_2S	223
VI-2	Methane-Sulfur Reaction	224

LIST OF FIGURES

SECTION VI - LITERATURE REVIEW

Figure	Title	Page
VI-1	H_2S Conversion Vs. Sulfur Loading	226

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION VI - LITERATURE REVIEW

1. Reaction of Hydrogen Sulfide and Sulfur Dioxide

1.1 Commercial Processes for H_2S Recovery

The original Claus process, developed at the end of the 19th century, consisted of catalytic vapor phase oxidation of hydrogen sulfide with air over a bauxite catalyst in a single reactor.

The Claus process as we know it today was developed in the 1930's(11) and consists of two steps. Usually one third of the feed gas containing 90% hydrogen sulfide is burned with air in a steam boiler forming sulfur dioxide and water. The SO_2 is then mixed with the balance of the hydrogen sulfide ($H_2S/SO_2 = 2$) and passed through a catalytic converter containing activated bauxite. The SO_2 and H_2S enter this first converter at 600°F and leave at 750°F. Seventy to eighty percent of the potential sulfur is formed in this converter and recovered by condensation. Unconverted gases leaving the condenser are then passed through a second converter and condenser. Sulfur scrubbing is employed to remove the last traces of sulfur. A 90+% sulfur yield is obtained in this manner.(28)

One modification employed on gases containing about 10% H_2S is to oxidize the H_2S directly to sulfur giving an 80% yield of sulfur. Some SO_2 is formed and this can then be catalytically reacted with H_2S in order to raise the over all yield.

The direct oxidation of H_2S is a highly exothermic reaction (ΔH = 145-173 Kcal/g-mole of H_2S).(21) The reaction of H_2S with SO_2 is also exothermic but to a lesser degree (ΔH = 21-35 Kcal). Therefore, this second reaction is preferred in sulfur preparation stage.

1.2 Application to Low SO_2 Concentrations

The application of the Claus catalytic process to the removal of low concentrations of SO_2 in stack gases raised a number of questions. It had to be determined whether the process would work with SO_2 concentrations below 0.5% by volume and still give high conversions. Also there was the possibility that the other gases present in the stack effluent might influence the reaction and these needed study. Munro and Masdin(26) conducted studies which answered some of these questions. They showed that the reaction took place at low concentrations. In addition, they established both theoretically and experimentally the effect of water vapor on conversion of H_2S in an inert gas stream. At 125°C even a water vapor content of 10% does not decrease equilibrium conversion below 90%, but at 225°C a water content of 5% results in an equilibrium conversion of 73%. Thus, in order to get high conversions on typical combustion flue gases, the temperature has to be kept below about 175°C. These workers also found that when operating at temperatures below 230°C, sulfur deposition deactivated the catalyst and consequently conversions steadily decreased with time.

1.3 Catalysts

Two catalysts were studied by Munro and Masdin. These were activated alumina B.S.S. 4-8 mesh (Peter Spence Actal) and 1/8 inch pellets of molecular sieve type 13X. Of the two, the molecular sieve type was found to be more effective.

The activated alumina catalyst trade-named Actal is also reported in a recent patent on waste gas purification issued to Peter Spence & Sons Ltd.(6) Studies were conducted on a typical flue gas composition of 6% H_2O, 4.8% O_2, 13.8% CO_2 and balance N_2. Conversions at only one temperature (100°C) were reported. The inlet concentrations of SO_2 and H_2S were approximately 0.25 and 0.50, respectively. The effect of space velocity was found to be small. 100% conversion was obtained for 1.65 seconds contact time. 94.4% was obtained at 0.3 second. In the examples cited in this patent, it was demonstrated that it is possible over a range of SO_2 concentrations to maintain the volume % H_2S in the effluent below 0.005. Data was presented which showed that the Actal is capable of taking up as much as 25% by weight of elemental sulfur before a significant fall-off is observed in the activity (see Figure VI-1). A system is proposed in this patent wherein the catalyst is continuously removed from the reactor and then regenerated and returned to the reactor.

The use of activated alumina for the H_2S reaction with SO_2 was patented by Audas & Thomas Ltd. in 1951.(3)

Conversions obtained for some of the more promising catalysts as given in Table VI-1.

Doumani(20) reported that effective catalyst regeneration from deposited sulfur was possible when the reaction tube and spent catalyst were raised in temperature to 500°C and held there for two hours. In this manner sulfur was vaporized from the catalyst and collected as molten sulfur. The last traces of sulfur can be stripped from the catalyst by means of an inert gas. Kerr(6) states that regeneration requires heating the sulfur-containing catalyst to a temperature preferably above the boiling point of sulfur (445°C) and in the presence of an inert gas. The sulfur released may be removed from the cooled gas stream by passing it through an electrostatic precipitator or a liquid sulfur scrubber.

1.4 H_2S in the Effluent

In the normal Claus process for H_2S recovery after reaction of SO_2 and H_2S and recovery of sulfur, the gases are usually passed to an incinerator, where any remaining H_2S is oxidized to SO_2 before discharging the gases to the stack. This is done because of the lethal qualities of even small concentrations of H_2S. In a thermal incinerator H_2S can be reduced to 10 PPM(27) or less and the effluent gas can then be sent up a sufficiently high stack.

1.5 Thermodynamics

A thermodynamic and chemical survey of the reactions involved in the reduction of SO_2 with H_2S as applied to the Claus Process has been published by Gamson and Elkins.(21) These theoretical considerations were extended by Munro and Masdin(26) to cover the conditions of power plant flue gases. Updated thermodynamic data was employed by them to calculate the theoretical equilibrium conversions of small quantities of H_2S with SO_2 over a range of temperatures. Munro and Masdin found the experimental results agreed very well with the theoretical predictions.

1.6 Reaction of H_2S and SO_2 in Solution

A number of British patents (1,4,5) were issued on a process for producing elemental sulfur by contacting gaseous H_2S and SO_2 with an aqueous solution containing an alkali metal sulfite.

2. Methane-Sulfur Reaction

2.1 Reactant Purity

The synthesis of carbon disulfide and hydrogen sulfide by the reaction of sulfur and methane has been studied by many workers. Specific studies have been made on the use of natural gas as the source of methane. The reactions of heavier hydrocarbons with sulfur have also been studied but it has been found that above C_4 the side reactions usually become an overriding factor. The use of methane minimizes the side reactions; consequently, studies have been conducted on the purification of natural gas. A patent has been issued on the incorporation of natural gas scrubbing to remove higher hydrocarbons prior to heating the reactants.(33) When the feed stock is natural gas containing primarily methane but which also contains a minor portion of hydrocarbons having three or more carbon atoms per molecule, the reaction with sulfur in the presence of a catalyst results in the formation of CS_2 and H_2S accompanied by formation of viscous, polymeric, sulfur-containing compounds. This is due to side reactions which cause degradation into tar and coke. These side reaction products deposit on the catalyst, causing decreased catalyst efficiency and difficulties in catalyst regeneration. Similarly, the presence of substantial amounts of hydrocarbons having four or more carbon atoms per molecule, will tend toward side reactions and tar formation.(58) In order to nullify the deleterious effect of side reaction products, a scavenging or agglomerating material has been studied.(53) For this same reason, studies of the non-catalytic reaction have also been made.(58,61) Substantial reduction in side reactions was reported when the catalyst was withdrawn from the reactor and regenerated at definite intervals.(55)

The sulfur purity is also important in avoiding polymeric side products. A number of patents have been issued on purification methods.(34,35,36)

2.2 Commercial Processes

A newly developed process, using gas oil or fuel oil in place of natural gas claims to have economic advantages over the use of natural gas to produce carbon disulfide and hydrogen sulfide.(67)

In the commercial process for the production of CS_2 from methane and purified natural gas, an over all yield of 90 to 95% based on sulfur is achieved by using 5 to 10% excess methane, at a temperature of 677°C and 30 to 40 psi. The H_2S produced in the commercial process goes to a sulfur recovery unit.(67)

2.3 Catalysts

The catalyst employed commercially for $CS_2 + H_2S$ production from methane and sulfur is activated alumina or clay. Any catalyst which promotes the formation of H_2S may be used but catalysts which produce the highest conversion of the reacting gases, at the lowest temperature are preferred because of the high corrosive action of sulfur vapors at high temperatures. Generally, catalysts such as silica gel, bauxite, certain catalytic clays and activated alumina, which give a high yield at temperatures below 700°C are preferred.(34) These catalysts may be promoted by small amounts of oxides or sulfides of the metals which are in groups V to VIII of the periodic table.(52) A list of the catalysts studied and the conversions obtained by various workers are given in Table VI-2.

2.4 Reaction Conditions

In general the reaction temperatures preferred are between 450° and 700°C. Below 450°C, the reaction rate is so low that only minor amounts of the sulfur and hydrocarbons react, and above about 675°C with stoichiometric amounts of sulfur present, the reaction becomes exothermic and is difficult to control.(59) More importantly at these temperatures sulfur vapor is highly corrosive. Data on corrosion rate increase with temperature increase has been reported.(57) Below a temperature of 750°C the reaction between sulfur vapors and hydrocarbon gas in the presence of a catalyst is endothermic and requires that the catalyst bed either be heated or that the gases be heated in the catalyst bed so as to support the reaction in the catalyst bed.(61) One patent was issued upon the claim that the heat was supplied to the catalyst by burning a combustible sulfur containing material. An example cited is the oxidation of hydrogen sulfide to sulfur which is highly exothermic.(52)

2.5 Liquid Phase

Studies of the liquid phase reaction where methane gas was bubbled through molten sulfur were conducted by Varga and Benedek.(62) A translation was made at Princeton Chemical Research of an article in Hungarian by these workers. This article indicated that at atmospheric pressure bubbling methane through molten sulfur at 400°C gave a partial conversion to H_2S without the concurrent CS_2 formation; however, when the reaction was studied at 200-400 atm. and 450 to 550°C, it was found that 100% conversion with stoichiometric production of CS_2 and H_2S can be achieved.

With regard to the liquid phase reaction, it is of interest to note that hydrogen will combine with molten sulfur when bubbled through it at 250 to 300°C under a pressure of 5 to 10 atm. Further, hydrogen when bubbled through boiling sulfur at atmospheric pressure will react provided a relatively large contact and reflux surface be maintained immediately above the sulfur; however, the conversion is low. The vapor phase reaction with various catalysts present (activated carbon, metal sulfides) gave as high as 98% conversion.(40)

A patent was issued to Thacker(46) on the reaction of methane with liquid sulfur. The procedure was to mix 2 to 20% by weight of catalyst with the sulfur and operate at temperatures above the boiling point, keeping the sulfur liquid by increasing the pressure. Thus, at 450°C a pressure in excess of 20 psi was employed whereas at 750°C the pressure is 400 psi. Raschig rings were employed as the contact surface. No data was given in the patent but high conversion of methane was implied.

2.6 Production of CS_2 Without H_2S

In the atmospheric reaction of methane with sulfur vapor at temperatures in excess of 1000°C, hydrogen sulfide becomes thermodynamically unstable and reverts to sulfur, the formation of CS_2 thus predominating.(63,37) De Simo showed that even as low as 800°C the reaction of CH_4 and sulfur producing CS_2 and H_2 predominates over that producing CS_2 and H_2S.(38) Previously, it had been demonstrated that the reaction of methane and hydrogen sulfide at temperatures above 850°C produced carbon disulfide and hydrogen,(37) but de Simo stated that there was no equivalency between the use of H_2S and the use of sulfur in the reaction since the equilibrium of the latter is much more favorable. A patent has been issued on the production of CS_2 from methane and sulfur or hydrogen sulfide at temperatures above 1100°C preferably above 1300°C, where the presence of oxygen does not result in the formation of carbonyl sulfide.(31)

Since a high reaction temperature was considered to be uneconomical, Thacker demonstrated that activated clay-type catalysts at temperatures below 700°C will produce per-pass conversion to CS_2 of over 90%.(41) In a later patent,(44) Thacker expresses a preference for bauxite. The advantages of using natural bauxite are also cited by Preisman.(45)

For the vapor phase reaction it is important to note the form of sulfur present. Near the boiling point at equilibrium approximately equal amounts of S_6 and S_8 are present in the vapor. At the temperature range of commercial feasibility for production of CS_2, S_6 and S_2 are the predominant species. S_1 is not present in appreciable quantities below 1000°C.

With regard to experimental considerations the sulfur vapors are extremely corrosive and will attack platinum thermocouple leads at 1000°C. At 600°C, stainless steel is corroded, but at rates which permit a reasonably long life for a reactor.(64)

Thacker practiced heating the sulfur to vaporization temperature, heating the methane to a temperature above the vaporization temperature of sulfur and then mixing the two. When the sulfur and methane are thus mixed, a temperature drop of about 30°C occurs due to further dissociation of sulfur. An additional drop of about 100°C occurs during the reaction. The practice was thus to initially operate near the maximum preferred temperature. In order to minimize the maximum operating temperature and consequently reduce corrosion, it has been proposed(57,59) to melt the sulfur (no vaporization), heat the methane while flowing through heated tubes in a furnace above the melting point of sulfur, mix the molten sulfur and heated gas by pumping the molten sulfur into the heated gas stream, and then superheat the mix and contact it with unheated catalyst.

2.7 Use of Hydrocarbons Other Than CH_4

The synthesis of carbon disulfide and hydrogen sulfide by the reaction of sulfur and hydrocarbons other than methane has also been studied. Studies have been reported on the use of acetylene,(30) propylene and butylene,(42) ethane and propane,(32) as well as heavier hydrocarbons.(47,48)

2.8 H_2S From $SO_2 + CH_4$

The production of H_2S from SO_2 and methane has also been patented. This reaction requires a very high excess of methane and temperatures greater than 600°C.

2.9 Adsorbents Containing Sulfur Treated with Methane to Recover H_2S

One reference was found.(29) Sulfur, produced from H_2S and SO_2 passed over Al_2O_3, is adsorbed on the Al_2O_3. Methane was passed over the Al_2O_3 at 440°C, and then brought into a reaction zone at 700°C. Conversion of over 40% was obtained.

In an article by Bacon & Boe,(70) brief mention was made of work done on the direct reaction:

$$CH_4 + 4S + 2H_2O \longrightarrow 4H_2S + CO_2$$

The bulk of this article was a discussion of the data obtained on the two stage reaction:

$$CH_4 + 4S \longrightarrow 2H_2S + CS_2$$

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2$$

With respect to the direct reaction, no data was presented but it was stated that some work was done by mixing water vapor, methane and sulfur vapor, and passing the mixture through a catalyst bed. With glass beads at 700°C, the reaction was described as very incomplete. With activated alumina at 600°C, only 0.2-0.3% CS_2 was reported present in the outlet gases, with a small amount of SO_2 due to the side reaction -

$$3S + 2H_2O \longrightarrow 2H_2S + SO_2$$

2.10 Kinetic Studies

A series of articles on the kinetics of the vapor-phase sulfur-methane reaction has been published by Smith and co-workers.

The first of these articles is by Fisher & Smith.(64) This paper discusses studies of the kinetics of the reaction of methane and sulfur vapor in a stainless steel reactor at temperatures from 550°C to 625°C, and at varying reactant ratios and space velocities. A second order reaction between methane and the S_2 species offers satisfactory kinetic interpretation of the experimental results and the reaction velocity constant (milliliters per gram mole-hour) is given by the equation:

$$k = 4.9 \times 10^{15} \, e^{\frac{-34,400}{RT}}$$

The reactor was completely packed with 7-mesh rock salt (inert).

A very good description of the experimental apparatus employed is provided in this paper. Important points cited were:

(i) The S vapors are corrosive at high temperature. In the neighborhood of 600°C stainless steel is corroded, but at rates which allow fair reactor life.

(ii) The unusual viscosity effects of liquid sulfur hinder conventional liquid rate measurements. Passage of sulfur vapor through a heated capillary tube offered the best solution.

The second paper in this series (Forney & Smith)$^{(65)}$ extends the study begun by Fisher & Smith to a catalytic reaction. The catalyst employed was 6-8 mesh silica gel. The catalyst bed depth, reactant mole ratio and feed rate were varied. The temperature was 600°C and the pressure 1 atmosphere. The kinetic data for the reaction correlated by assumption of a simple second order mechanism involving methane and diatomic sulfur -

$$r_c = k_c \cdot p_{CH_4} \cdot p_{S_2}$$

where $k_c = \dfrac{0.26 \text{ gram mole of } CS_2}{(\text{gram of catalyst})\ (\text{hr.})\ (\text{atm.})^2}$

The diffusional resistances effects were found to be negligible for the mass velocities employed.

The most recent paper in this series (Nabor & Smith)$^{(66)}$ extended the catalytic study to temperatures ranging from 550° to 700°C. The catalyst was again silica gel. It was found that a simple, second-order rate equation, based upon S_2 as the reactive species of sulfur, correlated the data at all temperatures. The reaction rate constant is given by the expression:

$$\log k_{c-c} = 10.9 - \frac{31,400}{2.303\ (RT)}$$

where $k_{c-c} = k_c\ (RT)^2$

and k_c = reaction rate constant for the catalyzed reaction (units to make rate units consistent with reaction mechanism).

Another paper concerned with the kinetics of this reaction is that by Thomas & John.$^{(63)}$ A thermodynamic study revealed maximum CS_2 production with negligible carbon deposition. Catalyst studies showed that at 400°C silica gel and vanadium pentoxide were superior to others studied and at this same temperature activated γ-alumina proved the least effective for this vapor-phase reaction. At 600°C all of the catalysts were fairly active. It was noted in this paper that the design equation formulated by Forney & Smith, while fairly accurate for silica gel, should not be employed when using a catalyst which displays retardation effects due to adsorption of reactant and product gases.

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TABLE VI-1

REDUCTION OF SO_2 WITH H_2S

Catalyst	% Conversion H_2S	Temperature, °C	Pressure, Atm.	Contact Time, Sec.	Space Velocity	Reference No.
Bauxite* (Activated)	--	--	--	--	--	28
Bauxite (12-20 Mesh)	99	93.3	1	--	550(1)	20
Aluminum Hydrate or Aluminum Oxide Hydrate	--	>300	--	--	--	9
Alumina (Activated) (Spence's Actal)	94	170	1	--	64(2)	26
Alumina (Activated) (Alorca)	100	93.3	1	--	650(1)	20
Alumina (Activated) (Spence's Actal)	100	100	1	1.65	--	6
Molecular Sieve (13X - 1/8 in.)	94	250	1	--	64(2)	26

* Commercial catalyst for Claus Process.

(1) Space Velocity - the total volume of reaction gases measured at 0°C and 760 mm Hg passing through a unit volume of catalyst per hour.

(2) Space Velocity - the volume of H_2S gas measured at 0°C and 760 mm Hg passing through a unit volume of catalyst per hour.

TABLE VI-2

METHANE-SULFUR REACTION

Catalyst	Percent Conversion (C) or Yield (Y)	Temperature, °C	Pressure, Atm.	Moles CH_4/S_2	Contact Time Sec.	Space Velocity*	Ref. No.
Tungsten	20-30 CS_2 (Y)	600-900	--	--	--	--	68
Chromium	20-30 CS_2 (Y)	600-900	--	--	--	--	68
Molybdenum	20-30 CS_2 (Y)	600-900	--	--	--	--	68
Silica Gel (Davidson 08-08-226)	90 CH_4 (C)	700	1	0.50	--	--	66
Silica Gel (6-8 mesh)	91 CH_4 (C)	600	1	0.33	--	--	65
Silica Gel	88 CH_4 (C)	600	1	--	10	--	53
Silica Gel	---	600-700	1	--	--	--	63
Silica Gel	73 CH_4 (C)	600	--	0.50	--	844	41
"High Silica Glass" (90% Silica) CoO Promoted	80 Nat. Gas (C)	620	1	≈ 1	--	890	56
Zirconium Oxide Gel (on Silica Gel or Act. Carbon)	89 HC (C)	550-700	2+	--	--	400	54
Metal Sulfides	60-80 S - CS_2 (C)	750-1000	1	--	.05-60	--	38
Clay Type	90 CS_2 (C)	500-700	--	--	--	--	69

(Continued)

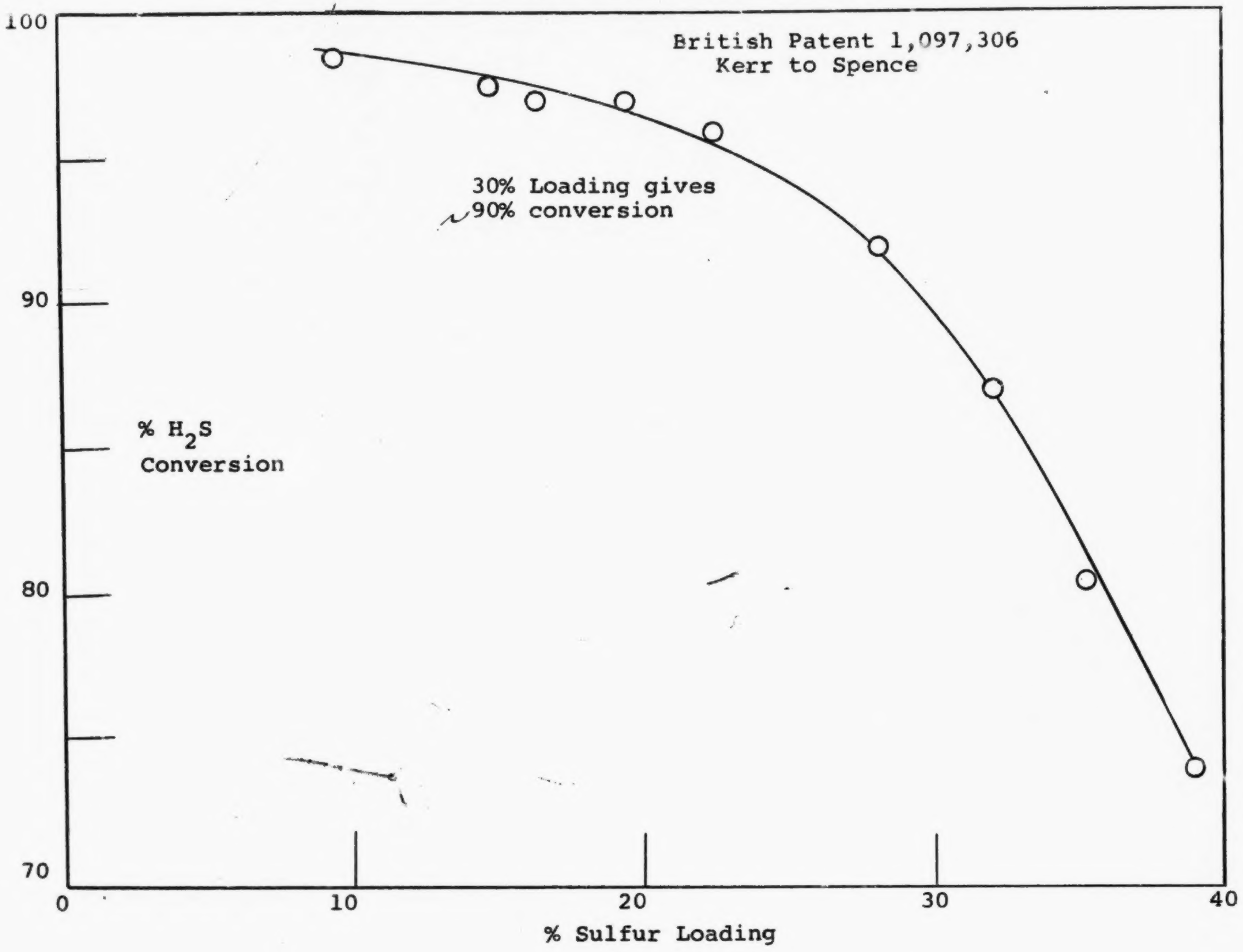
TABLE VI-2 (Cont.)

METHANE-SULFUR REACTION

Catalyst	Percent Conversion or Yield	(C) (Y)	Temperature, °C	Pressure, Atm.	Moles CH_4/S_2	Contact Time Sec.	Space Velocity*	Ref. No.
Vanadium Pentoxide	---		600-700	1	--	--	--	63
Bauxite	65 CH_4	(C)	600	--	0.48	--	850	41
Activated Bauxite	88-86 HC	(C)	600	4	--	--	400	55
Activated Alumina (200 mesh)	80 HC	(C)	600	2	--	--	--	55
Activated Alumina (Alorca)	55 CH_4	(C)	600	--	0.69	--	694	41
Commercial Activated Alumina	90-95 S	(C)	677	3	0.60	--	600	67
or Clay	91-92 S	(Y)						

* Space Velocity - the total volume of reaction gases measured at 0°C and 760 mm Hg passing through a unit volume of catalyst per hour.

FIGURE VI-1. H_2S CONVERSION VS. SULFUR LOADING



REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION VII

APPENDIX

TABLE OF CONTENTS

SECTION VII - APPENDIX

Page

1. Analytical Methods 231
   - 1.1 GC Methods for SO_2 Reduction Streams 231
   - 1.2 GC Analysis of H_2S Generator Streams 233
   - 1.3 Colorimetric Methods 233
     - 1.31 Absorption and Colorimetry of H_2S by the Methylene Blue Method 234
     - 1.32 Absorption and Colorimetry of NO and NO_2 by a Modified Saltzman Method 238
2. Pilot Plant Operation and Experimental Techniques 242
   - 2.1 Safety Procedures 242
   - 2.2 Operating Instructions 242
   - 2.3 Start-up and Operating Experiences 242
     - 2.31 Flue Gas Generation 243
     - 2.32 SO_2 Reduction 246
     - 2.33 Sulfur Stripping and Recovery and Catalyst Regeneration 247
     - 2.34 H_2S Generation 248
     - 2.35 Miscellaneous 250

LIST OF TABLES

SECTION VII - APPENDIX

Table	Title	Page
VII-1	Pilot Plant Safety Procedures	256
VII-2	Pilot Plant Operating Instructions - Flue Gas Generation System	261
VII-3	Pilot Plant Operating Instructions - H_2S Generation System	264
VII-4	Pilot Plant Operating Instructions - SO_2 Reduction System	267
VII-5	Pilot Plant Operating Instructions - Sulfur Stripping System	271
VII-6	Pilot Plant Operating Instructions - General Operating Notes	277
VII-7	Pilot Plant Operating Instructions - Method of Analysis of Gas Mixtures by Gas Chromatography	278
VII-8	Pilot Plant Operating Instructions - Process Description, Flowsheet Identification	283
VII-9	PCR Memo on Coal Combustion Operation	288
VII-10	Coal Characteristics	291

LIST OF FIGURES

SECTION VII - APPENDIX

Figure	Title	Page
VII-1	H_2S Absorption Assembly for Samples >100 ml.	292
VII-2	H_2S Absorption Assembly for Samples <100 ml.	292
VII-3	Apparatus for NO_x Sampling and Absorption	293
VII-4	NO_x Absorber with H_2S Trap	293
VII-5	Quantitative Transfer of Microvolumes of Pure NO	294
VII-6	SO_2 Reactor Temperature Profile	295

REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES BY REDUCTION TO ELEMENTAL SULFUR

SECTION VII - APPENDIX

1. Analytical Methods

1.1 GC Methods for SO_2 Reduction Streams

Gas chromatographic methods were developed for the analysis of mixtures containing N_2, O_2, CO_2, CO, H_2S, H_2O, and SO_2. The instrument employed was a Varian Model 202 gas chromatograph, equipped with a thermal conductivity detector (WX filaments) and linear temperature programmer. The column for CO_2, H_2S, H_2O, and SO_2 was 12-foot x 1/8-inch stainless steel packed with 50-80 mesh Porapak Q. The injector was maintained at 150°C, and the detector was 180°C; the He carrier gas rate was 40 ml./min.

CO_2, H_2O, and H_2S were eluted in that order isothermally at 30°C; the column was then either programmed, or rapidly heated, to 90°C to elute SO_2. At the low concentrations of H_2S and SO_2 normally analyzed - as low as 0.002% - it was found necessary to take certain precautions to prevent irreversible sorption of SO_2 in the GC. Fresh columns were normally heated at 230°C for 18 hours, and then conditioned with several 0.5 ml. injections of pure SO_2. Reconditioning with SO_2 was found necessary each time the column was heated over about 150°C.

Conveniently, N_2, O_2, and CH_4 were analyzed on a molecular sieve 13X column in series with the Porapak, across the detector.

The GC was generally calibrated using 0.25 ml. injections of the pure gases; peak areas were measured on a recorder equipped with a Disc integrator.

With care, H_2S and SO_2 could be detected at concentrations as low as 20 ppm, using 5 ml. sample injections. Analytical accuracy was estimated to be ± 0.5% or 0.1 µl of sample component, whichever was greater.

In the sulfur dioxide reduction runs, 5 ml. samples of the reactor feed and tail gas were periodically taken for analysis. The tail gas samples were taken hot using an insulated syringe preheated to 120°C, in order to prevent water condensation in the sample.

H_2S and SO_2 conversions were calculated based on carbon dioxide as an internal standard as follows:

Conversion of component i

$$= 100\% - \left(\frac{A_i}{A_{CO_2}}\right)_{\text{feed}} \cdot \left(\frac{A_{CO_2}}{A_i}\right)_{\text{tail gas}}$$

where Ai, A_{CO_2} are the GC peak areas of H_2S or SO_2, and CO_2, respectively.

In the SO_2 reduction runs in which CO_2 was present either in small or variable amounts, nitrogen was used as the internal standard.

1.2 GC Analysis of H_2S Generator Streams

The analytical equipment was generally the same as described in Section 1.1. Mixtures containing N_2, CO_2, H_2O, H_2S, COS, SO_2, and CS_2 were analyzed by isothermal column operation at 30°C at which temperature N_2, CO_2, H_2O, and H_2S were separated and eluted. The column was then programmed at 40°C per minute up to 175°C, for the elution of COS, SO_2, and CS_2.

Pure gas samples were used for calibration, except for water and carbon disulfide. Liquid water was injected as the H_2O standard, and a calibrated gaseous CS_2-N_2 mixture was used as the CS_2 standard.

Analytical accuracy was estimated to be generally better than 0.5% for each component determined.

1.3 Colorimetric Methods

Colorimetric analytical methods were developed for analyzing H_2S and NO_x, particularly at levels below 50 to 100 ppm. At these levels, the GC methods were not found to be sufficiently accurate.

Low levels of H_2S were analyzed by scrubbing a gas sample in a 1% aqueous $CdSO_4$ solution to precipitate H_2S as CdS. The CdS precipitate was then quantitatively converted to methylene blue, which was analyzed colorimetrically. The method is described in detail below. It was checked that SO_2 did not interfere at levels up to at least 2000 ppm. At H_2S levels over ∿100 ppm, the methylene blue method was found to agree with the GC method within a few percent or ∿30 ppm, whichever was greater.

The colorimetric method finally adopted for NO_x analysis was a modification of the Saltzman method, using a reagent recommended by S. Yanagisawa et al. (Bull. Chem. Soc. Japan 39, No. 10, pp. 2173-2187, 1966). We found that this reagent rapidly absorbed NO_2 when shaken with the gas sample, but very little NO was absorbed for the first few minutes. Therefore, gases containing

NO and NO_2 could be analyzed for NO_2 alone by shaking the gas volume briefly with the reagent, and then expelling the remaining gas. To analyze for NO, we found that NO could be oxidized to NO_2 if the gas sample contained at least 5% O_2, by shaking the reagent with gas sample frequently over a period of 60 minutes. Apparently, the oxidation is catalyzed by the absorbing reagent, since it was found to be complete down to <20 ppm NO after 60 minutes at room temperature. This corresponds to a much more rapid oxidation rate than predicted from the uncatalyzed rate data of J. H. Smith in "Selected Methods for the Measurement of Air Pollutants", U.S. Dept. of Health, Education & Welfare, May 1965, Cincinnati, Ohio, p. C-7.

The method is detailed below.

H_2S was found to interfere with the color reaction, but the interference was readily eliminated by passing the gas sample through an H_2S absorbent consisting of supported lead acetate plus glycerol. SO_2 did not interfere at levels up to at least 2000 ppm.

If the time allowed for NO oxidation was extended to 24 hours, the results were believed to be accurate for NO_x concentrations down to 5 ppm.

1.31 Absorption and Colorimetry of H_2S by the Methylene Blue Method

(i) Reagents

(a) H_2S Absorbent: 1% $CdSO_4$. Dissolve 10 g. of $CdSO_4$ in 1 liter of boiled deionized water.

Use boiled deionized water for the following preparations.

(b) Stock Amine Solution. Dissolve 27.2 g. p-aminodimethylaniline sulfate in 100 ml. of 1:2 H_2SO_4 (1 vol. H_2SO_4/2 vol. H_2O). STORE THIS SOLUTION IN A REFRIGERATOR.

(c) Test Amine Solution, ADMA. Dilute 25 ml. of stock amine solution to 1 liter with 1:2 H_2SO_4. STORE THIS SOLUTION IN THE DARK, OR IN A REFRIGERATOR.

(d) FeCl$_3$ Solution. 100 g. of FeCl$_3\cdot$6H$_2$O dissolved in 100 ml. of water.

(ii) Absorption

(a) For Gas Samples >100 ml. Place 10 ml. of 1% CdSO$_4$ solution in a midget impinger (Ace Glass Co. Cat. #753HO), and assemble an absorption train as in Figure VII-1. Sample the gas stream by inserting the 13 gage sampling needle through a septum-fitted sampling point. Adjust the pinch valves so that gas is drawn through the impinger at 100-200 ml/min. or less, and measure the total gas volume drawn on the wet test meter. For large amounts of gases which would be absorbed in the Mallcosorb trap (e.g., CO$_2$), either omit the trap or correct the measured volume for the concentration of the absorbed gases.

Use the following guide for gas sample volumes:

Conc. of H$_2$S in Gas Sample		Volume of Gas Sample
ppm	%	Basis ∿10 µl of H$_2$S
1	0.0001	10 liters
10	0.001	1 liter
100	0.01	100 ml.
1000	0.1	10 ml.
10000	1.0	1 ml.

After H$_2$S absorption, cap off the impinger until adding the color-developing reagents.

(b) For Gas Samples Less Than 100 ml. For samples less than 100 ml., the simplified absorption assembly in Figure VII-2 may be used. Attach the syringe to the absorption flask by sliding the syringe needle into the Teflon tubing. If the tubing I.D. is correct, a leakproof connection is easily obtained. Sample the gas stream by inserting the sampling needle through a septum-fitted sampling point, and manually withdraw the syringe plunger at a rate not greater than 100 ml/min. Remove the serum cap from the absorption flask, and keep the flask stoppered until the analysis.

(iii) Analysis.

To the midget impinger (ii)(a) or the 25 ml. volumetric flask from (ii)(b), add 1.5 ml. of test amine solution (ADMA), and immediately add 3 drops of $FeCl_3$ solution. Restopper the flask and shake briefly. After 5 minutes, transfer to a 50 ml. volumetric flask, and dilute to the mark with water. Let stand an additional 25 minutes.

Transfer to cuvettes and measure optical densities of the blue solutions at 670 mμ, using the red filter, on the Coleman Model 14 Spectrophotometer. The blue dye which the H_2S forms with the colorimetric reagent is methylene blue.

As the blank solution (zero optical density), use 10 ml. of 1% $CdSO_4$ solution, 1.5 ml. ADMA solution, and 3 drops $FeCl_3$, diluting to 50 ml.

If the optical densities of the test solutions are too high, they may be diluted quantitatively with a 1% $CdSO_4$ solution.

(iv) Standardization.

Two methods may be used to standardize the analysis, as follows:

(a) Standardization Based on a Calibration Gas Mixture.

Sample a suitable H_2S-containing calibration gas mixture, e.g., 1% H_2S in N_2, using the absorption assembly of Figure VII-2 containing 20 ml. of 1% $CdSO_4$. Withdraw sample sizes corresponding to 10 to 50 μl of H_2S (25°C, 1 at.).

Plot optical densities vs. H_2S sample sizes in μl. The curve should be fairly linear up to about 40 μl.

If the H_2S calibration gas analysis has not been certified by a reliable supplier, the calibration gas may be standardized against pure H_2S standards using a gas chromatograph.

(b) Standardization of the Colorimetric H_2S Analysis Against Sodium Sulfide

Concentrated Sodium Sulfide Solution

Prepare a 0.05 molar Na_2S solution by dissolving 12 g. of reagent grade $Na_2S \cdot 9H_2O$ per liter of boiled (air-free), cooled distilled water.

Standardization of Na_2S Solution

Pipet 25 ml. of the 0.05 molar Na_2S solution into a 250 ml. erlenmeyer containing a magnetic stirring bar. Then add simultaneously 25 ml. (pipet) of 0.1 N I_2 solution, and 10 ml. of 4 molar HCl (graduate cylinder). Immediately stopper the flask with a neoprene stopper, and stir 15 minutes.

Titrate with 0.1 N thiosulfate to the starch endpoint (i). To standardize the iodine, titrate 25 ml. with thiosulfate (ii).

$$M_{Na_2S} \text{ (Na}_2\text{S molarity)} = \tfrac{1}{2} \cdot \frac{N_{thio}\,(ml_{thio(ii)} - ml_{thio(i)})}{ml_{Na_2S}}$$

Working Sodium Sulfide Solution

Quantitatively dilute 10 ml. of the conc. Na_2S solution to 250 ml. with boiled (air-free) water. Each ml. of the working Na_2S solution is equivalent to:

$$\frac{10}{250} \times 10^3 \times 24.4 \quad M_{Na_2S}$$

or 975. × M_{Na_2S} µl of H_2S at 25°C, 1 at.

Standardization of Colorimetric Analysis

Pipet 1.0, 0.8, 0.6, 0.4, 0.2 ml. samples of the working Na_2S solution into 10 ml. of 1% $CdSO_4$ in a 50 ml. volumetric flask. Add the ADMA solution and $FeCl_3$ solution, and complete the colorimetric measurements.

Plot optical density vs. µl of H_2S (25°C, 1 at.) for the calibration curve.

1.32 Absorption and Colorimetry of NO and NO_2 by a Modified Saltzman Method: NO_x Concentrations of 5 to 1000 ppm.

(i) Reagents

(a) Absorbing and Colorimetric Reagent (Modified* Saltzman Reagent): Dissolve 0.05 g. N-(1-naphthyl)-ethylene-diamine dihydrochloride, 5 g. of sulfanilic acid, and 10 ml. of n-propanol in boiled deionized water, and dilute to 1 liter. STORE THIS SOLUTION IN THE DARK, PREFERABLY IN A REFRIGERATOR.

(b) Stock Sodium Nitrite Solution. Dissolve 2.03 g. reagent $NaNO_2$ in boiled deionized water and dilute to 1 liter.

(c) Diluted Standard $NaNO_2$ Solution. Dilute 1.00 ml. of stock $NaNO_2$ solution to 100.0 ml. with boiled deionized water.

(ii) Absorption and Analysis

Lightly lubricate a glass syringe with Dow-Corning silicone grease, and withdraw 10 ml. of the Modified Saltzman Reagent. Fit the syringe with a right-angle bent 2" x 20 gage stainless steel needle, as shown in Figure VII-3 or VII-4.

Keeping the syringe pointing vertically up, sample the NO_x-containing stream by withdrawing a suitable gas volume, e.g., as follows:

Approximate NO_x Concentration, ppm.	Gas Sample Volume, ml.
5 to 50	100
50 to 150	50 - 30
150 to 500	30 - 10
500 to 1000	5

---

*Continuous Determination of NO and NO_2 in the Atmosphere, S. Yanagisawa et al., Bull. Chem. Soc. Japan, 39, No. 10, (1966), p. 2174.

(a) NO_2 Only

To analyze for NO_2 only, immediately after withdrawing the gas sample into the absorption syringe shake the syringe once or twice and expel the gas sample. For more accurate work, the modified Saltzman reagent should be deoxygenated for 15 minutes or more, both before and after NO_2 absorption, by either (i) purging the solution with O_2-free N_2 using a gas scrubber, or (ii) vacuum-boiling the solution at room temperature.

After allowing at least 20 minutes for color development, transfer the solution to a 25 ml. volumetric flask, dilute to volume with water, and measure optical density at 550 mμ. As the blank solution (zero optical density), use 10 ml. of modified Saltzman reagent freshly diluted to 25 ml.

(b) $NO + NO_2$

To analyze for $NO + NO_2$, the absorption must be carried out in the presence of sufficient oxygen and long enough for essentially complete oxidation of NO to NO_2, and complete color development.

After withdrawing the gas sample into the absorption syringe, draw enough NO_x-free air or oxygen into the syringe to give at least 10% O_2 in the sample. Then cap off the syringe needle by means of a piece of silicone rubber. Shake the syringe frequently over a period of at least one hour for complete NO oxidation, NO_2 absorption, and color development. Complete the analysis as in (ii)(a).

(c) NO_x in the Presence of H_2S

H_2S bleaches the color produced by NO_2 in the modified Saltzman reagent; therefore H_2S must be removed prior to absorption of NO_x.

A convenient assembly for removing H_2S is given in Figure VII-4. It consists of a ¼" O.D. x 4" glass tube containing an H_2S absorbent, fitted to the absorption syringe by means of compression fittings, so that the only materials contacting the gas sample prior to NO_x absorption are stainless steel, glass, and the H_2S absorbent.

The H_2S absorbent is prepared as follows: 100 g. of 10-30 mesh high purity alpha-alumina carrier (SAHT-99, The Carborundum Company) is impregnated with 35 ml. of a water solution containing 2% lead acetate ($Pb(OAc)_2 \cdot 3H_2O$) and 2% glycerol. The absorbent is then dried 2 hours at 90 to 100°C.

Fill the absorption syringe with 10 ml. of modified Saltzman reagent, attach the H_2S absorbent, and withdraw an appropriate sample of gas to be analyzed. Flush the volume of the H_2S absorbent tube by withdrawing several ml. of NO_x-free air through the tube into the syringe.

Complete the analysis as in (ii)(a) or (ii)(b).

(iii) Standardization

Three different methods may be used to obtain a colorimetric calibration curve for the analysis, as follows:

(a) Standardization Based on a Calibration Gas Mixture

Obtain a mixture of NO_2 in N_2, containing 100 to 1000 ppm NO_2, with an analysis certified by a reliable supplier. Sample the gas and use the absorption and analysis method of (ii)(a), with appropriate sample volumes to give, say, 2, 4, 6, 8, and 10 µl of NO_2 (25°C, 1 at.).

Plot optical density vs. µl of NO_2. The calibration curve should obey Beer's Law within experimental error up to an optical density of at least 0.6.

(b) Standardization Based on Pure NO

Sample a lecture bottle of NO using a clean, dry 10-μl Hamilton fixed-needle syringe. Carefully transfer the gas sample to an inverted 25 ml. volumetric flask, containing 10 ml. of modified Saltzman reagent (remainder, air) and stopper with a silicone-rubber septum, as in Figure VII-5. Keeping the flask inverted, shake periodically over at least 1 hour. Then dilute the flask contents to 25 ml., and complete the standardization as in (iii)(a).

(Note: When transferring the NO from the microsyringe to the absorption flask, be sure to remove the last gas bubble from the needle tip by touching the tip to the wall of the flask.)

(c) Standardization Based on $NaNO_2$

Assume that for a standard $NaNO_2$ solution containing 20.3 μg of $NaNO_2$ per liter, each ml. of solution is equivalent to 10.0 μl of NO_2*. Pipet 0.2, 0.4, 0.6, 0.8, 1.0 ml. volumes of the standard $NaNO_2$ solution to 10 ml. of modified Saltzman reagent. Allow at least 20 minutes for full color development, and complete the standardization as in (iii)(a).

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*Selected Methods for the Measurement of Air Pollutants, U.S. Dept. of Health, Education & Welfare, Public Health Service, May 1965, page C-4

2. Pilot Plant Operation and Experimental Techniques

2.1 Safety Procedures

Safety procedures were drawn up and issued to the pilot plant operators. These procedures are reproduced completely as Table VII-1. Included are recommendations on housekeeping and safety equipment. Special attention is called to the hazards of fires, heat and chemical burns, electric shocks, and toxic chemicals. Descriptions of the physiological poisoning effects, prevention and treatment for exposure to hydrogen sulfide and sulfur dioxide gases are included.

2.2 Operating Instructions

Operating instructions for each section of the plant, and for the analytical systems were drawn up and issued to the pilot plant operators. These procedures are reproduced completely as:

Table VII-2	Flue Gas Generation System
VII-3	H_2S Generation System
VII-4	SO_2 Reduction System
VII-5	Sulfur Stripping System
VII-6	General Notes
VII-7	Gas Analyses
VII-8	Process Description and Flowsheet Identification

2.3 Start-up and Operating Experiences

The primary operating problems were encountered in:

(a) Feeding small quantities of pulverized coal.

(b) Design and operation of the coal combustion unit.

(c) Handling sulfur at low flow rates.

These problems were all solved during the operating period.

2.31 Start-up and Operating Experiences - Flue Gas Generation

Although the coal combustor was originally scheduled for delivery in early December 1968, it was not received until mid-February 1969. Initial start-up attempts were made within two weeks.

The start-up procedure called for lighting a gas pilot tip externally, and thrusting the pilot through a one-inch aperature in the refractory furnace liner to ignite the main gas burner. The purpose of the main gas burner was to preheat the refractory prior to starting combustion of pulverized coal.

Initial attempts to light the main gas burner were unsuccessful because the pilot flame was extinguished when it was inserted into the furnace. The flame safety controls, fuel mixer and gas pressure regulators were checked but were found to be functioning. Since the pilot flame appeared very weak, a pilot tip with larger orifices was ordered.

New attempts to ignite the main gas flame were unsuccessful. The larger pilot flame still blew out. No difference was noted when the exhaust gases were vented to the atmosphere or through the catalyst bed.

Representatives of Ionics visited PCR and after observing several start-up attempts, and after making numerous adjustments to the controls, decided to take the burner section back to the factory for further testing. A few days later PCR was informed that the burner was operating. A PCR representative visited the General Ionics plant in Pittsburgh in mid-March. The burner was set up on a test stand. The burner was lit several times without much difficulty. The Ionics people explained that the main burner nozzle originally used had been undersized. The result was that the flame was not able to propagate back to the nozzle because the velocity of the fuel-air mixture was too great. Unfortunately, because the gas burner nozzle was threaded into a one-inch pipe which made up the core of the burner assembly, it was not feasible to install a larger nozzle. Rather, the nozzle was removed entirely, and this change made it possible to light the burner.

A representative of North American Manufacturing Company (who supplied most of the burner controls) visited while the tests were in progress. He noted that the flame was somewhat unstable even with the nozzle removed. Premix burners of the type used in the installation function properly only when sized to provide a slow, lazy flame. While in Pittsburgh, the PCR engineer also visited the Bureau of Mines, Bruceton, Pennsylvania development center. A four lb./hr. coal combustion unit was observed; BuMines commented on their experience gained in operating the small coal combustor. The highlights of these discussions are included in a trip report attached as Table VII-9.

The burner was installed again by representatives of General Ionics. Careful adjustment of the gas-air ratio to a gas rich condition made it possible to keep the burner lit as long as flue gas was by-passed directly to the vent. When gases were vented through the reducing reactor and the main vent closed, the flame went out. The apparent reason was that when the combustion chamber pressure increased, the gas-air ratio was changed. Although the change in the gas-air mixture was slight, it was sufficient to upset the delicate balance in the basically unstable flame.

The gas burner was obviously still too unreliable, and the North American Manufacturing Company was asked to make recommendations. They advised that the only way to make the gas flame stable was to eliminate the undersized gas burner from the system and install a new gas burner of adequate size. They also strongly urged modifications to insure safe operation, specifically installation of automatic electrical ignition to replace the manual pilot and a purge timer to insure that unburned gas was removed from the combustion chamber before ignition was attempted. Additional safety devices were also suggested: (1) a rupture disk of 6.5 psi burst pressure to prevent over-pressurization of the combustion chamber, (2) a pressure switch operated running light to indicate safe combustor outlet line pressure, and (3) a pressure switch operated running light and flame shutdown feature to indicate operation of the cooling air fan. These recommendations were accepted and delivery of the required parts was promised for early May delivery.

While awaiting delivery of these parts, the top of the furnace was modified to accept the 2-inch pipe connection required. When this was completed, the furnace was fired using the smaller gas burner and coal combustion was tried. The first few attempts were unsuccessful because the firebrick was not sufficiently hot and because the pulverized coal was feeding unevenly.

Short periods of coal burning were achieved when predried coal was supplied to the hopper of the coal feeder. However, the coal transport line between the hopper and the burner and the annular space in the burner carrying coal and primary (transporting) air to the burner ring frequently became plugged with coal. When this occurred, it was necessary to shut off the coal feeder at once, to prevent coal from backing up to the feeder and bending the feed screw. After plugging, the burner and transport line had to be laboriously disassembled for cleaning.

To minimize the occurrence of coal pluggage, the feeder was relocated to a position directly over the centerline of the burner and the central pipe originally intended for the main gas/ air flow was used to feed coal to the burner tip. Coal was thereby gravity fed to the burner and primary air merely helped in dispersing the coal being transported to the tip. A 55-gallon drum equipped with external hot oil tracing was installed to permit pretreatment of the coal. These changes permitted uninterrupted coal combustion for periods of up to ten hours duration.

The new gas burner parts were received on May 12th and were in operation on May 16th. The flame was quite stable and was capable of preheating the firebrick in about 4 hours compared to a heat-up time of 16 to 24 hours with the old system.

Occasionally, the orifices of the gas burner became plugged with carbon and coal pyrolyzed in the burner passages, both of which required shutdown for cleaning. In spite of these difficulties, start-up of the combustor was considered complete and operation was possible for extended periods.

After several hours of coal combustion, a deposit of partially burned coal and ash was observed at the bottom of the combustion chamber. The deposit was fairly hard, porous and contained up to 60% of combustibles upon ignition. This material, similar to coke, was apparently formed when part of the coal fed was heated to the plastic range (600-900°F) and formed agglomerates. In order to maximize the efficiency, coal was not introduced until the firebrick was cherry red in color. In addition, the secondary air supply was preheated to permit earlier ignition of coal. While some coke deposits remained, the build-up never exceeded a depth of 12 to 18 inches and operation did not seem to be impaired.

The characteristics of the coal are detailed in Table VII-10.

2.32 Start-up and Operating Experiences - SO_2 Reduction

The SO_2 reactors performed as expected; only minor problems of a mechanical nature were experienced.

Alcoa F-1 activated alumina catalyst was used as the first catalyst charge. A -3/8 +1/4" granular fraction was screened from the mixture and charged to the reactors. The second catalyst charged was Linde 13X (1/8" x 1/4" extrusions).

Pressure drop measurements were not easily attainable as the taps plugged often with sulfur. Several data points were obtained on the alumina, and generally agreed with predicted drops for the slightly less than 3/8" particles. Because of the other pressing problems, this was not pursued further during the short operating period.

Temperature control was provided by controlling power input to the beaded heaters in response to a thermocouple in the catalyst bed. Initially, the heaters were all connected to a single source. This resulted in a severe temperature profile in the bed ($<$250 to $>$370°F). The heaters were then separated and provided with individual power supplies to minimize the profile. As seen in Figure VII-6, the new profile was much flatter.

Leakage from the reactor flanges was frequent (perhaps because of temperature cycling) until some sections of piping were replaced by stainless steel flexible hose.

Sulfur plugging was experienced at the reactor inlets. It was eliminated by removing unreacted sulfur from the H_2S stream and by moving the mixing point (of the H_2S with the flue gas) closer to the catalyst bed.

2.33 Start-up and Operating Experiences - Sulfur Stripping and Recovery and Catalyst Regeneration

Although the stripping system still required further experimentation, it functioned well. Most of the problems encountered were equipment problems rather than process problems.

Several breakdowns of the stripping gas blower were experienced, accompanied by overheating. After several rebuilding experiences, it was discovered that the blower speed was set at the factory substantially higher than design. This resulted in excessive back pressure (due to undersized piping) and machine overheating. No difficulties were encountered after correction of the speed.

Corrosion of the blower was not a problem as anticipated and the machine showed no signs of severe corrosion at the end of the program. It was still operating perfectly. During the breakdown periods, stripping gas was provided from bottles of nitrogen and hydrogen sulfide.

The stripping gas dryers were not used during the program.

The stripping gas heater functioned as designed. A burn out of one-half of the six heating elements was experienced. Probably due to sulfide corrosion, the burn out had no significance since the heating element temperatures were far in excess of temperatures which would be experienced commercially.

The sulfur condenser was designed for ease of operation in the pilot plant. It was admittedly not a commercially feasible design, but sulfur collection is a well-known practice, and not in need of exploration. The condenser performed adequately in the pilot plant. The collection efficiency was generally found to be better (as measured by carry over) when the wall were kept at a temperature above the melting point of sulfur.

2.34 Start-up and Operating Experiences - H_2S Generation

One of the objectives of the program was to define suitable materials of construction. Although a rupture in the H_2S reactor was experienced, the alumina lined steel reactor design is believed to be suitable.

The reactor consisted of a mullite tube cemented to the inside of a Type 310 stainless steel pipe with flanged connections at both ends. The reactor performed well for about two months. However, the reactor walls then failed during operation, spilling gas into the hooded area. After the reactor cooled, inspection revealed a large hole through the shell and the liner near the midpoint of the furnace. Initially, it was not clear whether the failure resulted primarily from corrosive failure of the liner or mechanical failure of the liner and shell due to excessive temperatures or both.

A study of the temperature recorder charts showed that on several occasions the temperature measured within the catalyst bed had reached temperatures approaching 2000°F for short periods during start up the preceding two weeks. A record of the temperature of the outside reactor wall was not available but it was certainly much higher because of the electric tube furnace type of heating. It was concluded that the excessive temperature caused the rupture. The location of the control thermocouple was then changed so that it was in contact with the outside of the reactor shell. The control point was set at the temperature required to maintain the desired internal reaction temperature of 1300°F. No further reactor failures occurred after the control method was modified.

Commercially, the occurrence of this type of excessive temperature is not possible. The reaction is exothermic, but not sufficiently so to cause a runaway. In fact, adiabatic operation is contemplated. The pilot reactor in effect was not adiabatic, but had large heat losses, requiring continual external heating to maintain the reaction. This external heating was the cause of the excessive temperature.

Several Type 316 stainless steel thermowells failed as a result of corrosion during the first few weeks of operation. The wells were constructed from 1/4-inch o.d. tubing and were located at the centerline of the reactor. Corrosion appeared most severe in that portion of the tube that was imbedded in the catalyst. Life of the wells varied from a few days to two weeks.

Vycor glass wells were tried without much greater success. A mild steel well coated with Nucerite (Pfaudler, Rochester, N.Y.) failed in a few days. New wells of high purity recrystallized alumina and Alonized steel tubes (heat treated in contact with aluminum powder forming an aluminum alloy with the base metal) were ordered.

At this time the method of temperature was changed to minimize the occurrence of excessive temperatures. The stainless steel thermowell installed at this time remained intact throughout the remainder of the program. The Alonized steel and alumina tubes were never tested.

Corrosion of alloy steels was expected to be severe in the atmosphere present in the hydrogen sulfide reactor. Although stainless steel seems to have some useful life at 1300°F, failure occurs rapidly at higher temperatures. Alumina-lined steel appears to be resistant.

After the original Fluid Metering sulfur pump was replaced by the BIF piston pump, no difficulties in pumping sulfur were experienced unless plugs developed downstream. The pump was protected against damage in this event by shear pins which were easily replaced.

2.35 Start-up and Operating Experiences - Miscellaneous

The beaded electric heating wires consisted of nichrome wire insulated with ceramic beads. These heaters were used throughout the process wherever high temperature (>300°F) heat was required. The beaded heaters were coiled around the pipe or vessel to be heated and insulated to prevent heat loss. Power, either 120V or 240V, was supplied through powerstats. In some cases, power input was regulated by means of a temperature controller.

The heaters tended to burn out when operated at excessive temperatures, but they generally were a satisfactory source of high temperature heat.

Plugging of lines with pulverized coal residue and sulfur presented a serious problem. While considerable improvement was realized as a result of operating experience, care was still required to prevent plugging.

The design of the flue gas generation system anticipated the need for adequate fly ash removal. A cyclone separator was installed to remove large particles and line filters were provided to remove particles of one micron size or smaller. In practice, the cyclone separator removed little solid matter from the gas stream, presumably because very little material of large particle diameter was present. The line filters were effective in removal of quantities of fine ash and partially burned coal particles from the flue gas before it entered the reduction reactors.

Occasionally, dust escaped the line filters, causing plugging of the flue gas lines entering the reactors, the catalyst support screens and, in one instance, the lower part of the catalyst bed as well. Possible explanations include 1) inadvertent opening of the filter by-pass valve, 2) imperfect gasketing of the filter element to the filter body, and 3) passing of very fine particulate matter through the filter fabric.

At times, frequent removal of the filter elements for cleaning was required due to condensation of moisture from the gas. This caused a slimy residue to block the pores of the filter fabric. This problem was overcome by addition of steam tracing to the flue gas line from the cyclone separator to the filters.

When pipelines became sufficiently coated to restrict the flow of gas, it was necessary to dismantle them for cleaning.

Even more prevalent than line plugging caused by coal dust was that caused by sulfur. The condition was more prevalent because sulfur was handled throughout the process. The key to handling sulfur was keeping the pipe uniformly hot; localized cold spots rapidly caused plugged lines.

When sulfur is handled as a liquid, the temperature throughout the pipeline must be maintained between 250° and 300°F. This covers the range between the melting point and the temperature where sulfur enters a region of rapidly increasing viscosity. Viscosity peaks at about 370°F and becomes easily flowable again as temperature approaches the boiling point. Hot oil tracing, cemented directly to the pipe to be heated and supplied with oil from an oil reservoir maintained at about 290°F, was the most convenient means of keeping liquid sulfur flowable. However, extreme care was required to eliminate all cold spots at bends, tees, elbows, and wherever tracing was difficult.

Wherever it was desired to keep sulfur in the vapor phase, it was necessary to maintain the pipeline at or near the boiling point of sulfur, 830°F, even if the sulfur concentration was quite low. This was accomplished by wrapping the pipeline with electrical heaters of beaded nichrome wire. The pipeline and heaters were then covered with insulation to minimize heat losses. While electrical resistance heaters tend to exhibit hot spots at the points of highest watt density or lowest heat loss, plugging of lines resulting from condensation of sulfur vapor could not occur as long as the coldest part of the line was kept above the dew point of sulfur vapor. The usual reasons for plugging in a line carrying sulfur vapor were 1) insufficient power input to the heater, 2) a burned out conductor, or 3) insufficient insulation. When pluggage occurred, disassembly and cleaning was usually required.

Since most of the lines were of small size, from 1/4 to 1 inch in diameter, the metal wall and the contents of the pipe were capable of storing very little heat and tended to lose temperature rapidly when a process upset occurred. Therefore, constant surveillance was required to detect cold spots before trouble developed. The following locations were the major plugging areas:

- Sulfur pump discharge line.
- Tee where natural gas and steam were mixed with sulfur before entering the reactor.
- H_2S generation reactor outlet line; if cold spot was found in time, heat was applied and sulfur was blown back through the pipeline with nitrogen pressure.
- SO_2 reactor ball valves; these were difficult to heat uniformly because of their irregular shape, often plugged; valves at lower end of reactor were most often affected because their location made them more difficult to drain.

- Flue gas inlet; sulfur left from stripping process added to fly ash in flue gas created problems.
- SO_2 reactor catalyst support screen; same problem as flue gas inlet.
- H_2S-flue gas mixing tee; problem caused by unreacted sulfur from H_2S reactor; partial remedy was installation of sulfur disengaging pot (maintained at 290°F) at H_2S reactor outlet; since plugging was not entirely eliminated, the line carrying H_2S from the generator to the reducing reactor was heated more intensely to about 800°F.
- Sulfur condenser inlet from SO_2 reactor; during the initial part of the stripping operation, gas containing a high concentration of sulfur vapor and probably droplets of liquid sulfur passed through this line; heat added to the pipe from the electrical tracing was at times insufficient to vaporize the sulfur.
- Sulfur condenser drain; the condenser heating mantles were turned on between stripping cycles; sulfur melted from the walls was drained through an oil traced ball valve beneath the condenser; the valve, located at a low point, was very susceptible to plugging.
- Sulfur condenser outlet line; this line was traced with hot oil at 290°F; provided the condenser operated at design efficiency, the dew point of sulfur vapor in the condenser outlet was lower than 290°F and sulfur would not condense; when changes in stripping gas flow, exit gas temperature and other variables occurred, sulfur sometimes condensed and plugged the line from the sulfur condenser outlet to the sulfur knock-out drum.

- Sulfur knock-out drum; since the drum was cooled by external cooling water coils, the inlet and outlet connections were cold and very susceptible to plugging.

Gas under pressure in various parts of the process leaked to the atmosphere of the room whenever pipe fittings became loose. Leaks were most often found around flanged pipe connections which were sealed by relatively soft gasket material. Anticipating this problem, flanged connections were minimized in assembling the piping.

Leaks were easily detected by the characteristic odors of H_2S and SO_2. If readily found, the leaking joint was tightened without interrupting the process. Sometimes it was necessary to shut down the process and pressure test in order to find the leak.

Leaks more frequently occurred around the large flanges of the reducing reactors and the sulfur condenser. Other locations where frequent leaks occurred were the flanged pipe sections connecting the ball valves which controlled the gas flows entering and leaving the reduction reactors.

Because of sulfur deposition on the seats or due to failure of the seats from excessive temperature, these ball valves sometimes developed internal leaks. Under these conditions, gas leaked from the stripping gas system to the flue gas side or the reverse depending upon which pressure was higher. Unusual variations in flow during operation as well as routine pressure testing indicated the presence of internal leaks. Seal replacement was required to correct the problem.

Piping surrounding the hydrogen sulfide generator had to be maintained free of leaks because 1) the gas was very toxic due to high H_2S concentration, and 2) since the flows were small, a considerable fraction of the reactants or products might have been lost as the result of minor leaks. Fortunately, since the line sizes were small, tubing connections were made using compression fittings which seldom leaked.

The incinerator utilized to insure the effluent from the pilot plant contained no H_2S was never studied in detail. No odors in the area of exhaust were detected, but none were detected after the catalytic elements were removed.

TABLE VII-1

PILOT PLANT SAFETY PROCEDURES

Good safety practices must be observed at all times to prevent accidents.

Practice Good Housekeeping

Keep work areas clear of equipment and records which are not then in use.

Guard Against Burns

The hot oil system, electrical heating elements, molten sulfur and hot gases can inflict serious burns unless proper caution is used.

Electrical Shocks

Both 120 and 240 volt power is used to operate controls and motors in the pilot plant. Disconnect power and check terminals with voltage tester before repairs or adjustments are attempted.

Toxic Materials

Both hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) are dangerous materials. Avoid breathing air contaminated with these gases. See safety bulletins on these gases, following pages. Read Chemical Safety Data Sheets published by Manufacturing Chemists Association.

Safety Equipment Includes:

H_2S tester: MSA Universal test kit for H_2S

Explosimeter: Indicates dangerous concentrations of explosive gases.

Gas Masks: With chin type cannister for acid gases and organic vapors.

Air Respirator: Attach to air line should emergency rescue be required.

TABLE VII-1(CONTINUED)

PILOT PLANT SAFETY PROCEDURES

Fires

Natural gas and hydrogen sulfide (H_2S) are both combustible gases. Sulfur will burn as a vapor when mixed with air. The liquid will also catch fire when melted in an open beaker if too much heat is applied. The combustion characteristics of these materials are:

	Minimum Ignition Temperatures	Limits of Flammability in Air, %
H_2S	558°F (292°C)	4.3 - 45.5
Nat. Gas	1170°F (632°C)	5.0 - 15.0

Fire extinguishers are of two basic types:

1) dry chemical and 2) carbon dioxide (CO_2). Both are suitable for extinguishing fires caused by flammable liquids or electrical fires.

For small fires, which can be easily extinguished, it is recommended that a CO_2 extinguisher be used (dry chemical is a mess to clean up).

TABLE VII-1 (CONTINUED)

PILOT PLANT SAFETY PROCEDURES

SAFETY BULLETIN

HYDROGEN SULFIDE (H_2S)

Description: Colorless gas, flammable, offensive odor (rotten eggs).

Toxicology:

Irritant: Immediate irritation of eyes, irritation of throat after several minutes.

Asphyxiant: Takes place in stages dependent upon concentration and exposure period. Results in paralysis of the respiratory center.

Systemic Effects: See Table A for detail of likely effects at various concentrations and exposure times. NOTE THAT EXPOSURE TO CONCENTRATIONS AS LOW AS 0.01% for 8 to 48 HOURS CAN CAUSE DEATH. EXPOSURE TO VERY HIGH CONCENTRATIONS RESULTS IN IMMEDIATE DEATH.

Important: While H_2S has a pronounced odor even at very low concentrations, a person loses his ability to detect the odor after a short period of continuous exposure. Therefore, you must act to correct the leak and/or clear the area when H_2S odor is first detected.

First Aid Treatment:

Remove person immediately to fresh air. Apply mouth to mouth resuscitation if breathing has stopped. For eye irritation, remove to darkened area and apply ice compresses to eyes and forehead. Consult a physician.

Preventive Measures:

1. Maintain adequate ventilation.
2. Minimize unnecessary risk by avoiding operating procedures which might vent H_2S containing gases into the room.

TABLE VII-1 PILOT PLANT SAFETY PROCEDURES

TOXICITY OF HYDROGEN SULFIDE TO MEN

H_2S PER CENT	0-2 MINUTES	2-15 MINUTES	15-30 MINUTES	30 MIN-1 HOUR	1-4 HOURS	4-8 HOURS	8-48 HOURS
0.005 .010				Mild conjunctivitis; respiratory tract irritation.			
0.010 .015		Coughing; irritation of eyes; loss of sense of smell.	Disturbed respiration; pain in eyes; sleepiness.	Throat irritation.	Salivation and mucous discharge; sharp pain in eyes, coughing.	Increased Symptoms.*	Hemorrhage and death.*
0.015 .020		Loss of sense of smell.	Throat and eye irritation.	Throat and eye irritation.	Difficult breathing; blurred vision; light shy.	Serious irritating effects.	Hemorrhage and death.*
0.025 .035		Irritation of eyes; loss of sense of smell.	Irritation of eyes.	Painful secretion of tears; weariness.	Light shy; nasal catarrh; pain in eyes; difficult breathing; conjunctivitis	Hemorrhage and death.*	
0.035 .045		Irritation of eyes; loss of sense of smell.	Difficult respiration; coughing; irritation of eyes.	Increased irritation of eyes and nasal tract; dull pain in head; weariness; light shy.	Dizziness; weakness; increased irritation; death.	Death.*	
0.050 .060	Coughing; collapse and unconsciousness.*	Respiratory disturbances; irritation of eyes; collapse.*	Serious eye irritation; light shy; palpitation of heart; a few cases of death.*	Severe pain in eyes and head; dizziness; trembling of extremities; great weakness & death.*			
0.060 .070 .080 .10 .15	Collapse; *unconsciousness;* death.*	Collapse; *unconsciousness;* death.*					

*Data secured from experiments on dogs which have a susceptibility similar to man.
Bulletin 231 of the Bureau of Mines Report, 1925
Courtesy of HOUSTON ATLAS, INC.

TABLE VII-1

PILOT PLANT SAFETY PROCEDURES

SAFETY BULLETIN

SULFUR DIOXIDE (SO_2)

Description: Colorless gas, non-flammable, pungent odor.

Toxicology:

Irritant: Highly irritating to the eyes, throat and lungs, even in small concentrations.

Asphyxiant: Results in paralysis of the respiratory center.

Systemic Effects: Gas is so irritating that it provides its own warning of toxic concentrations. Concentration of 0.015% is so irritating that it can be endured for only a few minutes. Concentrations of 0.05% produce a sense of suffocation with the first breath. Concentration of 0.005% to 0.010% is considered to be the maximum that is permissible for periods of 30 to 60 minutes. HIGH CONCENTRATIONS MAY CAUSE DEATH.

First Aid Treatment: Remove person immediately to fresh air. If the eyes are irritated, flush with quantities of warm water.

Preventive Measures:

1. Maintain adequate ventilation.
2. Minimize unnecessary risk by avoiding operating procedures which might vent SO_2 containing gases into the room.

TABLE VII-2

PILOT PLANT OPERATING INSTRUCTIONS

FLUE GAS GENERATION SYSTEM (SEE FIGURE IV-10)

Start Up

1. Close the switch valves (SV's) on the SO_2 reactors and open reactor bypass valve V-53, and open valves through one of two fly ash filters (e.g., V-90 and V-91).
2. Bring the catalytic incinerator to operating temperature.
3. Fill hopper on coal feeder to operating level. Tighten down lid.
4. Close FV-1 so that gas does not enter combustion zone.
5. Open V-82 and close V-83 and admit air to gas burner through FV-3 adjusting to flow desired on FI-3.
6. Open gas cock valve V-97 and start natural gas booster. Adjust to desired pressure. Open WV-99 to admit cooling water to gas cooler.
7. Open V-100 and start cooling air fan. Open WV-86 admitting water to the burner cooling ring and WV-87 to the trim cooler.
8. Open V-98 and ignite gas pilot.
9. Furnace must be preheated by burning natural gas before feeding coal. Admit gas to desired flow rate for ignition by opening FV-1. If flame safety controls sense a safe start up condition, gas flame can be ignited by operating latch valve EV-85.
10. After furnace has been preheated, pressurize coal feeder by opening FV-2 and adjusting to desired flow on FI-2. Position V-80 and V-81 as required to balance pressure between coal hopper and discharge pipe.

TABLE VII-2 PILOT PLANT OPERATING INSTRUCTIONS

11. Adjust coal feeder to desired feed rate setting and start coal feeder. If coal does not feed or if screw begins to bind, shut off immediately and adjust.

12. When coal flame is established, turn off gas by closing FV-1. Open V-83 to direct secondary air to coal burner and close V-82.

13. The oxygen monitor is used to determine the efficiency of combustion. Open valve V-95 to blow down condensate and close immediately. Open V-96 and adjust until TI-10 reads 220°F. DO NOT EXCEED THIS TEMPERATURE. Oxygen concentration is read directly from the indicator scale.

14. Observe flue gas temperatures at TI-80, TI-81 and TI-31 and adjust to desired flue gas inlet temperature by adjusting V-100 and WV-87.

During Operation

15. If flame goes out during operation, check to see if coal is still feeding. Then shut off coal feeder. Check level of coal in coal hopper and refill if necessary. Re-establish gas flame as in start up instructions and after furnace is again at operating temperature, start feeding coal again.

16. At intervals the coal hopper must be refilled. This will be done only after shutting down flue gas generator at first but will eventually be done by blowing coal into the hopper under pressure so that combustion will not be interupted.

TABLE VII-2 PILOT PLANT OPERATING INSTRUCTIONS

Shutdown

17. Open reactor by pass valve V-53 and close reactor switch valves.
18. Shut off coal feeder and close V-80.
19. Allow air to flow through V-81 and V-83 for 5 min. to evaporate condensate and permit combustor-cooler unit to cool. Then shut off FV-2 and FV-3.

NOTE: Replace septums in sample fittings S-1, S-2, S-9 and S-10 when flue gas generator is shut down. Replace septums in sample fittings S-5 and S-6 when both the flue gas generator and the H_2S generator are shut down.

TABLE VII-3 PILOT PLANT OPERATING INSTRUCTIONS

H_2S GENERATION SYSTEM. (SEE FIGURE IV-17)

Start Up

1. Close V-38 and V-39 located near SO_2 reactors. Also close V-40, V-41, V-50 and V-51 if bottled H_2S is not being used. Open H_2S by-pass valve V-52 to main stack gas vent header.
2. Bring the catalytic incinerator to operating temperature and turn on hood fan.
3. Set hot oil temperature controller to 330°F. When oil temperature is above 100°F, start hot oil pump with suction valve V-22 and recycle valve V-25 open. Throttle V-25 to obtain 40 psig on PI-24 at pump discharge. Open V-24, V-26, HV-20 and HV-21 to heat sulfur feed system to 290°F (do not exceed 300°F).
4. When sulfur feed system is at operating temperature, add molten sulfur to sulfur feed tank from covered stainless steel beaker maintained at 175°F in a heating mantle. Fill to the mark.
5. Fill burette on water feed pump to top graduation mark.
6. Adjust H_2S reactor feed preheater and furnace heater controls to obtain the required reaction temperature (ca. 1300°F).
7. Open FV-4 and adjust natural gas flow rate as desired by observing FI-4 (natural gas booster must be operating).
8. When natural gas flow rate has been established, open burette stopcock and start water feed pump and adjust feed rate as required for the reaction.

TABLE VII-3 PILOT PLANT OPERATING INSTRUCTIONS

9. If sulfur feed lines and pump body are at the correct temperature, there should be noticeable torque transferred to the pump shaft and pump will run smoothly. Adjust pump to required feed rate. Analyze reactor outlet sample from S-4; H_2S and CO_2 concentrations show whether sulfur is feeding properly.

10. If necessary, readjust feed preheater and furnace temperature controls until desired bed temperature is reached.

11. When proper reaction temperature is established and flows of water, sulfur and natural gas have been established, withdraw a sample from S-4 and analyze. A sample may be withdrawn from S-3 to determine water/natural gas feed ratio.

12. Analyze a sample from S-6 to determine whether H_2S is being removed from the gas being vented. Raise incinerator bed temperature to lower the concentration of H_2S in the vent gas.

13. After flue gas flow to one of the SO_2 reactors has been established and bed temperature (ca. 260°F) has been reached, open the H_2S feed valve (V-38 to feed SO_2 reactor #1; V-39 to feed SO_2 reactor #2). Then close H_2S by-pass valve V-52. H_2S and CO_2 from the H_2S generator will now be mixing with flue gas entering the bottom of the SO_2 reactor which is being started up on reduction cycle.

During Operation

14. Adjust flow rates of materials fed as well as temperatures of the preheater and catalyst bed during the run as required to maintain specified conditions.

TABLE VII-3 PILOT PLANT OPERATING INSTRUCTIONS

15. Fill sulfur feed tank with molten sulfur and water pump burette as required during the run. Accurate weighings must be done to determine the exact quantity pumped over a given time period.
16. Analyze samples from S-3 and S-4 as required.

EMERGENCY PROCEDURE

Should an odor of H_2S develop, find the leak and tighten fittings while wearing a gas mask. If the leak cannot be maintained within the hood, shut off all feed to H_2S reactor, cool the feed preheater and furnace and clear the room. (After the feed has been shut off, the reduction of SO_2-containing flue gas can be continued by switching to bottled H_2S provided no noticeable H_2S odor persists.

USE GAS MASK AT FIRST SIGN OF H_2S LEAK. H_2S (ROTTEN EGG ODOR) KILLS SENSE OF SMELL. DO NOT ATTEMPT ANY LEAK REPAIR OR ANY OTHER ADJUSTMENT TO THIS SYSTEM UNLESS A SECOND OPERATOR IS PRESENT AND ALERTED TO PROBLEMS. SEE SAFETY PROCEDURES FOR FURTHER INFORMATION.

Shutdown

17. Open V-52 by-passing H_2S to the incinerator. Then close the H_2S feed valve to the SO_2 reactor (V-38 if SO_2 reactor #1 is being shut down).
18. Shut off water feed pump and sulfur pump. Turn temperature controls for the H_2S reactor feed preheater and furnace to the lowest setting. Leave FV-4 on for about 5 minutes so that flow will clear the catalyst bed of sulfur, water and products of reaction.
19. When H_2S reactor has cooled sufficiently, stop natural gas flow by closing FV-4.

NOTE: Replace septums in sample fittings S-3 and S-4 whenever the reactor is shut down.

TABLE VII-4

PILOT PLANT OPERATING INSTRUCTIONS

SO_2 REACTION (REDUCTION) SYSTEM. (SEE FIGURE IV-14)

Start Up of SO_2 Reactor #1

1. Flue gas generator (coal burner) and H_2S generator (H_2S reactor) must be started up prior to starting the SO_2 reduction unless synthetic flue gas (air and SO_2) and/or H_2S from the gas bottle is used.
2. Assuming the catalyst in SO_2 reactor #1 has been stripped and regenerated (stripping gas compressor is off), it is now ready for reduction of SO_2. Adjust TC-1 to the desired reaction temperature (ca. 260°F).

NOTE: Since flue gas will normally be switched from the other reactor (in this case, reactor #2), you will probably find the switch valves (SV's) in the opposite position from that shown in Figure 1 (open circle in valve drawing means valve is open; filled in circle in valve drawing means valve is closed).

3. Place the three-way valves for the manometers, 3V-42, 3V-43, 3V-44 and 3V-45 in the closed position (handles turned half-way) to prevent blowing out fluid due to pressure surges.
4. After making sure stripping gas compressor is off, close SV-30, SV-32, SV-35 and SV-37, so that flue gas will not be mixed with stripping gases.
5. Open SV-31 and SV-33 admitting flue gas to reactor #1. SV-34 and SV-36 will normally be open too so that for a short time flue gas will be passing through both reactors.
6. Close SV-34 and SV-36, so that flue gas is now flowing only through SO_2 reactor #1.

TABLE VII-4 PILOT PLANT OPERATING INSTRUCTIONS

NOTE: Since flue gas must be vented while the coal burner is operating, by pass valve V-53 must be opened first, if for any reason flue gas must be shut off to both reactors at once.

7. Readjust TC-1 to obtain the desired catalyst bed temperature in SO_2 reactor #1.
8. Carefully turn the three-way valves for reactor #1, 3V-42 and 3V-43, to the reaction position (handles pointing toward the reactor), while observing the liquid in manometer DPI-1 to see that it is not blown out.
9. Carefully open V-38 admitting H_2S and CO_2 from the H_2S generator to SO_2 reactor #1. Then close H_2S by pass valve V-52. Observe pressure on PI-50 to be sure that H_2S line entering the reactor is not blocked by sulfur solids in the line. Reduction of SO_2 in the flue gas with H_2S will now be underway. (If the H_2S generator is not operating, H_2S can be fed from the H_2S bottle through V-40).
10. When proper reaction temperature is established, withdraw samples from S-9 and S-2 and analyze.

During Operation

11. Adjust temperature of the catalyst bed during the run as required to maintain steady conditions. Flow of flue gas will depend on the proper amounts of coal and air being fed to the furnace. Flow of H_2S will depend on the rate at which sulfur, water and natural gas are being fed to the H_2S reactor and at what temperature the H_2S reactor catalyst bed is maintained.
12. Analyze samples from S-1, S-2, S-9 and S-10, as required. Also analyze samples from S-5 and S-6 to monitor the efficiency of incinerator operation.

TABLE VII-4 PILOT PLANT OPERATING INSTRUCTIONS

EMERGENCY PROCEDURE

Should an odor of H_2S or SO_2 develop, put on a gas mask and tighten fittings which are leaking. If the leak is serious, put on gas mask, shut off both H_2S reactor feed pumps, shut off motor switches, pull all plugs on the front of the panel board and clear the room. SEE TABLE IV-11 FOR FURTHER INSTRUCTION ON H_2S LEAK EMERGENCY.

Switching Procedure (Start up of SO_2 Reactor #2)

When analysis of samples from S-2 shows that the catalyst in reactor #1 no longer has the required activity as shown by increasing SO_2 and H_2S content, the SO_2-containing flue gas and the H_2S feed must be switched to reactor #2, which will have been stripped of sulfur, reactivated and maintained at reaction temperature. The switching procedure is the start up procedure in reverse. First open H_2S by-pass valve V-52 and close H_2S feed valve V-38 to reactor #1. Then:

1a. Flue gas generator and H_2S generator will already be operating.

2a. Catalyst in SO_2 reactor #2 has been prepared for reduction of SO_2. Adjust TC-2 to the desired reaction temperature.

3a. Place the three-way manometer valves in the closed position (handles turned half-way, 3V-42, 43, 44, 45).

4a. After making sure stripping gas compressor is off, close SV-30, SV-32, SV-35 and SV-37.

5a. Open SV-34 and SV-36 admitting flue gas to reactor #2, while SV-31 and SV-33 remain open.

6a. Now close SV-31 and SV-33 so that flue gas is flowing only through SO_2 reactor #2.

7a. Readjust TC-2 to desired catalyst bed temperature.

TABLE VII-4 PILOT PLANT OPERATING INSTRUCTIONS

8a. Carefully turn three-way manometer valves 3V-44 and 3V-45 in the reaction position (handles pointing toward reactor).

9a. Carefully open V-39 admitting H_2S and CO_2 from the H_2S generator to SO_2 reactor #2. Then close H_2S by pass valve V-52, observing PI-50 for indication of line pluggage. Reduction of SO_2 is now underway in reactor #2.

10a. When proper reaction temperature is established, withdraw samples from S-10 and S-2 and analyze.

Shutdown

13. Shut down the H_2S generator and the flue gas generator as previously described (let air blow through the catalyst bed for 5 minutes).

14. Set temperature controller for minimum temperature setting.

15. After air from combustor cooler unit has either been shut off or by-passed through valve V-53 and stripping gas compressor has been shut off, switch valves around SO_2 reactors may be closed.

TABLE VII-5

PILOT PLANT OPERATING INSTRUCTIONS

SULFUR STRIPPING SYSTEM. (SEE FIGURE IV-15)

Start Up for Stripping of Sulfur From SO_2 Reactor #2

1. The gas used for stripping (removing sulfur) will be either nitrogen or a mixture of nitrogen and H_2S. Since stripping gas is re-used (re-cycled), it is held in the stripping gas system ready for use.

2. Assuming the catalyst in SO_2 reactor #1 has been stripped (sulfur removed) and regenerated (brought back to original activity), the stripping gas compressor will have been shut off.

NOTE: When the catalyst in SO_2 reactor #2 becomes too inactive for efficient reduction of SO_2 to sulfur, switch the flue gas and H_2S feed streams to SO_2 reactor #1 (see operating instructions for SO_2 Reaction System). SO_2 reactor #2 is now ready for stripping.

3. The three-way valves 3V-44 and 3V-45 for manometer DPI-2 should be in the closed position (handles turned half-way).

4. Check to see that SO_2 reactor switch valves SV-30, SV-32, SV-34 and SV-36 are closed. Open switch valves SV-35 and SV-37.

NOTE: Follow the route the stripping gas will take while flowing through the stripping gas system. We will assume that moisture is being removed from the stripping gas in gas dryer #1. When you follow the flow lines from Figure IV-15 and pick them up again in Figure IV-14, YOU WILL SEE THAT THE STRIPPING GAS SYSTEM FORMS A CONTINUOUS LOOP. This means that once the valves are properly set and the stripping gas compressor is running, the same gas is being pumped around the loop being alternately heated and cooled at different points in the loop. GAS DRYER #2 IS NOT A PART OF THE LOOP because a new supply of air is being brought in and then vented from the system.

TABLE VII-5 PILOT PLANT OPERATING INSTRUCTIONS

5. The hot oil system must be operating (see instructions for H_2S Generation System). Open valves HV-70, HV-48 and HV-49 to heat tracings at the lower ends of the SO_2 reactors and the sulfur condenser. Check to be sure the lines get hot. Close sulfur drain valves V-68, V-46 and V-47.
6. Crack open water valve WV-73 to the sulfur knock out drum.
7. Check to see that gas dryer switch valves SV-60, SV-62, SV-64 and SV-66 are closed. Open SV-61 and SV-63 (SV-65 and SV-67 will also be open if gas dryer #2 is being regenerated).
8. Open V-69 and FV-5. Check oil level in the stripping gas compressor (fill only to middle of sight glass). Turn belt by hand to see that it turns freely. Start compressor.
9. Carefully close V-69 while checking discharge pressure PI-67. Compressor should run smoothly with a minimum of noise. If it does not, make the required adjustments.

NOTE: Compressor must not be allowed to overheat. A temperature of 230°F is not considered excessive.

10. Adjust FV-5 to obtain required stripping gas flow as shown on FI-5.
11. Carefully turn the three-way manometer valves for reactor #2 to the stripping position (handles pointing toward the wall) to prevent blowing out fluid.
12. Set temperature controls as follows:

    TI-62 - Sulfur knock out drum outlet (ca. 150°F)
    TR-7-pt. #9 - Gas dryer #1 (ca. 150°F)
    MTC-8 -pt. #7 - Stripping gas primary (ca. 600°F)

TABLE VII-5 PILOT PLANT OPERATING INSTRUCTIONS

TC-65 - Chromalox heater (ca. 900°F)*
TI-66 - Stripping gas secondary (ca. 950°F)(powerstat only)
TR-7-pt. #5 - SO_2 reactor #1 bed (ca. 950°F)

* Maximum allowable temperature is 1000°F. Do not operate without stripping gas flow.

NOTE: Sulfur stripped from the catalyst should begin to appear on the walls of the sulfur condenser. During initial operation, sulfur collected will be removed at the end of the run by applying hot air to the outside of the condenser or by scraping the inside surface or both. After the cooling characteristics of the condenser are determined by operating the system, it may be possible to apply hot oil or electrical tracing to the condenser to remove the sulfur collected on the walls.

During Operation

13. Adjust temperatures and stripping gas flow as specified.

EMERGENCY PROCEDURE

Should an odor of H_2S or SO_2 develop, put on gas mask and tighten fittings which are leaking. If the leak is serious, shut down entire system (as described in Table IV-11) and clear the room. SEE TABLE IV-12.

14. Crack open V-68, V-46 and V-47 as required during the run and drain molten sulfur into a tared stainless steel beaker. Reweigh the beaker and record weight of sulfur collected.

TABLE VII-5 PILOT PLANT OPERATING INSTRUCTIONS

NOTE: If an N_2/H_2S mixture has been used for stripping, catalyst reactivation is not required. If the stripping gas was nitrogen, treatment of the catalyst with H_2S is required following the stripping operation. In the latter case, the required amount of H_2S would be fed to reactor #2 from H_2S bottle via FI-30 to V-41 and released to the incinerator by opening V-51. The best way of handling catalyst reactivation by H_2S treatment will be determined early in the pilot plant program.

Withdraw and analyze samples from S-7 as required to determine concentration of H_2S and water in the stripping gas.

Shutdown

15. Set Chromalox heater control, primary, and secondary (Table IV-13, item 12) stripping gas controls to lower settings as required to cool catalyst bed gradually to 260°F over a period of one to two hours. When gas has cooled to 400°F, gradually add water to the hot stripping gas line through the humidifier water pump where it will be vaporized to steam. Alternately, steam can be added from the steam generator. The water added will be absorbed by the catalyst to replace water lost from the catalyst during stripping. Shut off water or steam feed and allow stripping gas to flow for at least 10 minutes to remove water from the lines.
16. When reactor #2 has been cooled sufficiently, shut off stripping gas compressor and close SV-35 and SV-37. Reactor is now ready for use in the next SO_2 reduction cycle.
17. Drain or otherwise remove sulfur collected in the sulfur condenser and the drain legs under the SO_2 reactor. Weigh and record weight of sulfur collected.

TABLE VII-5 PILOT PLANT OPERATING INSTRUCTIONS

NOTE: If it is necessary to open a pipeline or a vessel to remove sulfur or for any other reason, first it will be necessary to purge the equipment with nitrogen or air to remove H_2S and SO_2 which may be present (nitrogen must be used on a hot system which contains sulfur or H_2S to prevent oxidation (or combustion) to form SO_2 with heat release.

18. Remove sulfur collected in the demister, sulfur knock out drum and the filter at the K-O drum outlet. Where sulfur is collected on a replaceable filter element or glass wool, the weight of sulfur will be obtained by weighing the element before and after stripping and calculating the difference.
19. Replace glass wool in demister and place a clean filter element in the filter in preparation for the next sulfur stripping cycle. Replace septum in S-7.

Reactivation of the Gas Dryers

The gas dryers contain an absorbent used to pick up excess moisture from the stripping gas to prevent unwanted chemical reaction of water with sulfur in the SO_2 reactor catalyst during stripping. "Molecular sieves" will be used as the absorbent. When the sieves in dryer #1 become saturated with water, they must be dried (regenerated) with hot air to remove the moisture. While this is being done, the stripping gas is put through the dryer #2 by changing the position of the switch valves. The procedure is similar to that required for switching flue gas from one SO_2 reactor to the other. To regenerate the sieves in dryer #2:

20. Check to see that switch valves SV-60, SV-62, SV-64 and SV-66 are closed. Open SV-65 and SV-67.
21. Open FV-7 to the required air flow rate as shown on FI-7.

TABLE VII-5 PILOT PLANT OPERATING INSTRUCTIONS

22. Adjust temperature controls as follows:

    MTC-8-pt. #4 - Regeneration air primary (ca. 450°F)

    TC-5 - Gas dryer #2 (ca. 450°F)

    Regeneration air secondary (as required by adjusting powerstat).

23. When regeneration is complete, close FV-7 and lower temperature controls to minimum settings. Then close SV-65 and SV-67. Sieves are now ready for use in the next stripping gas drying cycle.

TABLE VII-6

PILOT PLANT OPERATING INSTRUCTIONS

GENERAL OPERATING NOTES

The shift leader is responsible for safety, protection of equipment and record keeping on his shift.

All operators are encouraged to maintain good housekeeping standards and to constantly be on the alert to upgrade the equipment by making necessary repairs or additions, as required. Weighings and analyses should be done with maximum accuracy. Data records should be complete and readable.

Care of Equipment

1. Valves should be closed without excessive force to prevent galling the seat and plug. When valves are opened, turn until valve handle stops, then return valve handle a half turn toward the closed position to prevent strain on the packing (this does not apply to ball valves).

2. Use anti-sieze compound on stainless steel fittings before tightening threads.

3. Always open valves on discharge side of pumps and compressors before running as this equipment is not designed to run against excessive pressure.

4. Keep moving equipment properly lubricated according to manufacturers instructions. In general, oil levels must be checked once each shift and grease fittings lubricated twice each week.

TABLE VII-7

PILOT PLANT OPERATING INSTRUCTIONS

METHOD OF ANALYSIS OF GAS MIXTURES BY GAS CHROMATOGRAPHY

The method employed in the analysis of the feed and tail gas samples is gas chromatography.

The system works in the following manner:

With the carrier gas - helium - that is admitted into the instrument, the gases to be analyzed flow into the separating column towards a detector; the detector senses the heat-conductivity of each gas in the sample and the values are recorded on the recorder.

CARE OF INSTRUMENT

To maintain the chromatograph functioning properly, it is IMPORTANT that the following "Start-Up" and "Shut-Down" procedures be observed.

START-UP PROCEDURE

Drawings of the Aerograph 200 (pgs. F-4 and F-5) show controls which are numbered as follows:

Part No.

1. Open valve on gas cylinder to start helium flow to the rotameters. LEAVE FILAMENT POWER OFF.
2. Unscrew cap from injection port 'A'; install new septum.
3. Using bubble-o-meter, check helium flow.
4. IF HELIUM FLOW STILL SHOWS ON ROTOMETERS, turn filament power on.
5. Turn oven power on. DO NOT LEAVE OVEN HEATING WITH HOOD OPEN.
6. Return attenuator from zero to position 1.
7. Close hood; raise oven temperature to 120°C for 30 minutes to purge system.
8. DO NOT ADJUST CONTROLS NUMBERED 8.

TABLE VII-7 PILOT PLANT OPERATING INSTRUCTIONS

SAMPLE PROCEDURE

To obtain reproducible results the following sampling and injection techniques should be employed.

Obtaining Sample

a. Turn on recorder chart switch and set attenuator.

b. Hold the injection syringe by the barrel with the left hand, allowing the measured area to be fully visible; the right hand works the plunger.

c. Inject the needle into the sample port with the plunger of the syringe in completely.

d. With the left hand firm, pull a sample and allow the ground-line marked on the plunger to reach about 1/4" above the maximum volume line. After five seconds the plunger is pushed in completely.

e. Part d is repeated three times, but on the third occasion the syringe with the sample is removed from where the sample was taken with the plunger about 1/4" above the maximum volume line.

Injecting Sample

f. The volume of sample is measured by aligning the ground line on the plunger with the desired volume on the calibrated scale of the barrel.

g. The thumb of the right hand resting lightly on the flanged head of the plunger prevents the plunger from popping out suddenly due to positive pressure through the needle.

h. All forward action is done with the left hand when the syringe with the sample is injected into the injector #2; be sure to hold as little pressure as necessary with the right thumb on the plunger during injection. Failure to do so would result in a loss of sample volume.

i. After the needle is completely injected, the sample is then gradually pushed into the column by pushing in the plunger.

TABLE VII-7 PILOT PLANT OPERATING INSTRUCTIONS

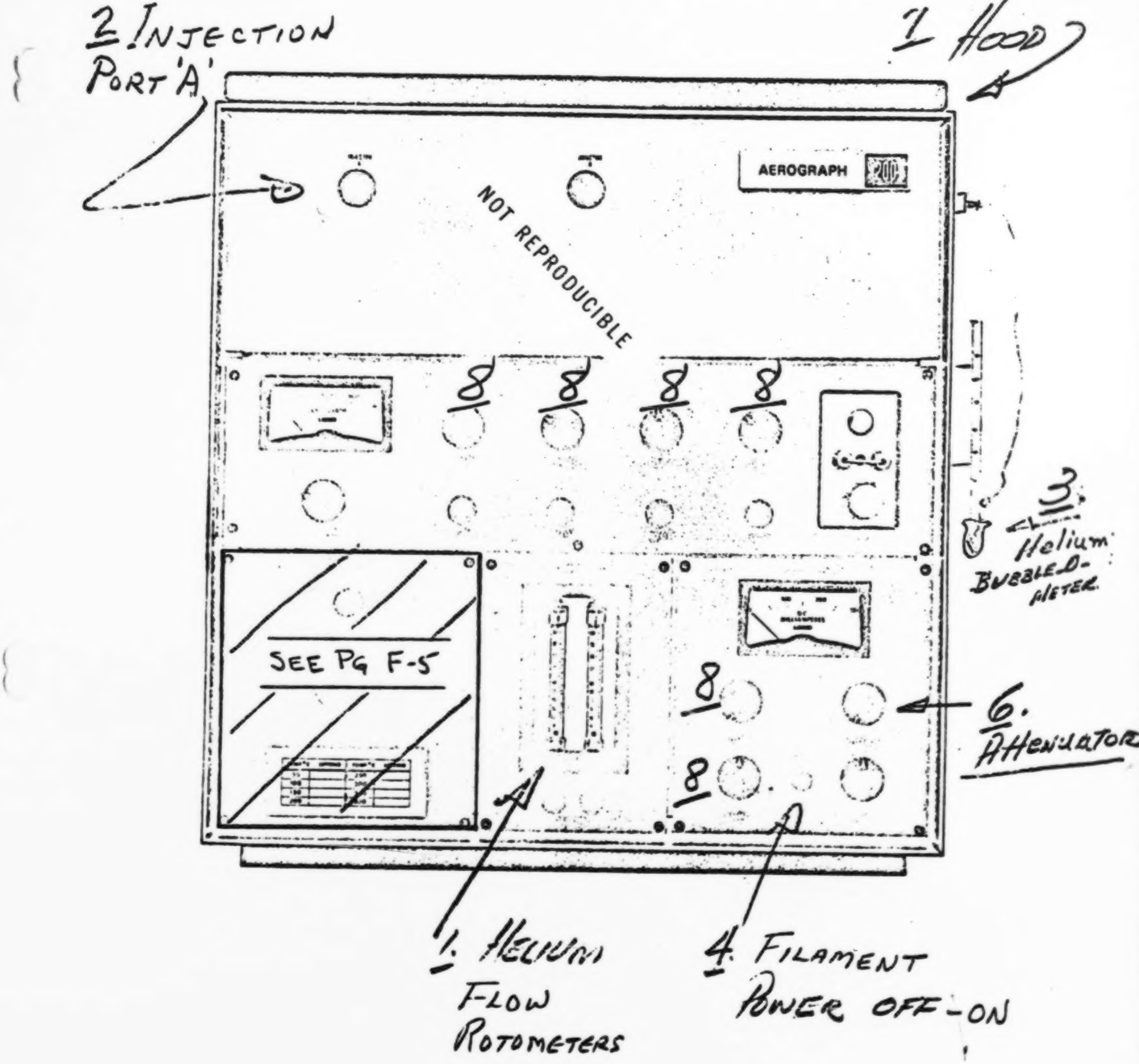
j. The syringe is maintained in the injector for about two seconds after injection is completed. Care should be taken not to bend and increase the size of the hole made by the needle; the sample would immediately escape and be lost should this happen.

k. When all the peaks are recorded, the chart switch is turned off and the column is allowed to cool in preparation for the next injection.

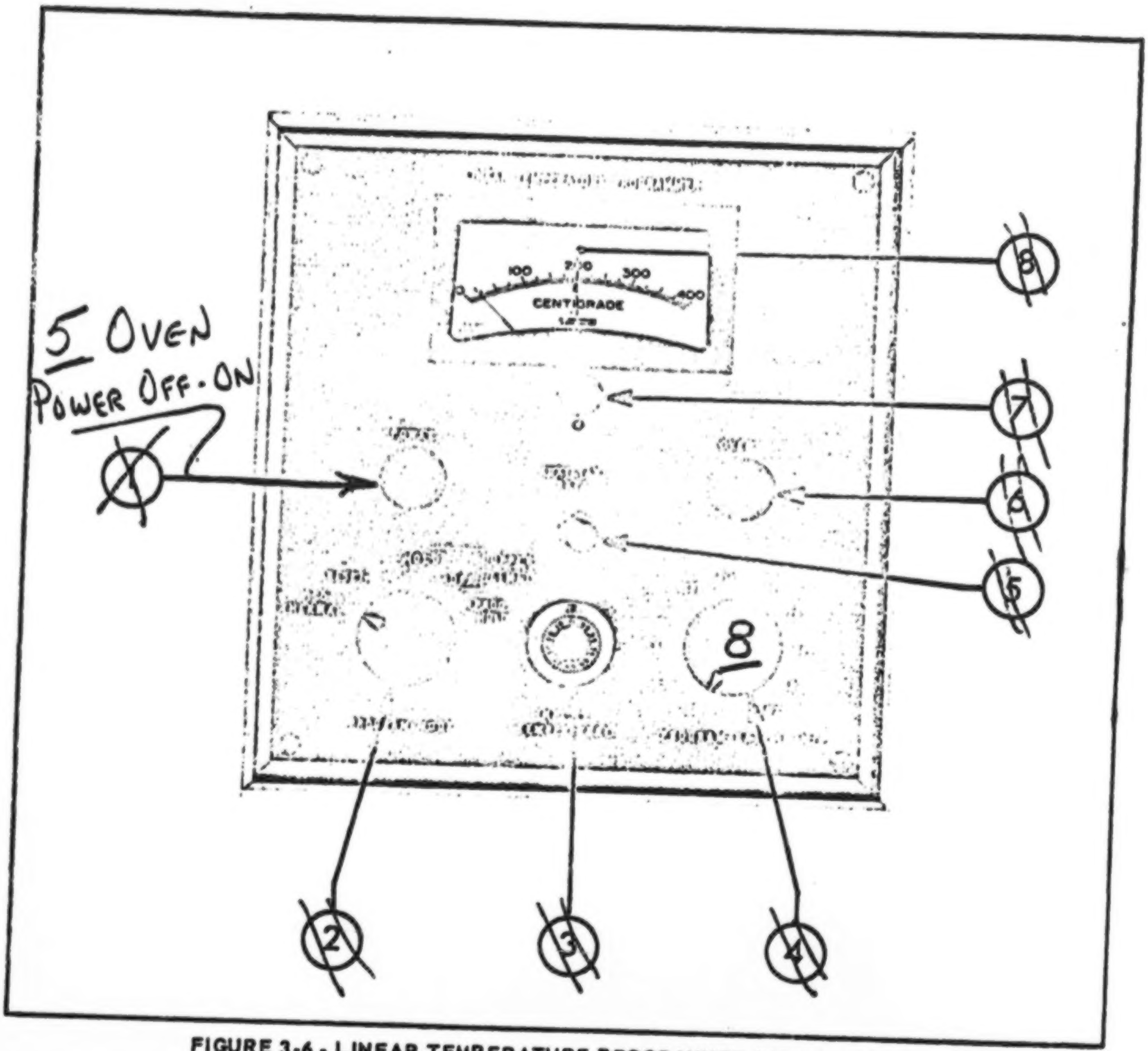
SHUT-DOWN PROCEDURE

1. Close hood (#7)
2. Set attenuator to zero (#6)
3. Cut out filament-power (#4)
4. Cut out power to oven (#5)

TABLE VII-7 PILOT PLANT OPERATING INSTRUCTIONS


2. Injection Port 'A'
7 Hood
AEROGRAPH
202
NOT REPRODUCIBLE
8
8
8
8
3. Helium Bubble-Meter
SEE Pg F-5
8
6. Attenuator
8
1. Helium Flow Rotometers
4. Filament Power off-on

Aerograph Model 202-B Gas Chromatograph



5 Oven
Power Off-On

FIGURE 3-6 - LINEAR TEMPERATURE PROGRAMMER (MODEL 202-1)

TABLE 3-6 - LINEAR TEMPERATURE PROGRAMMER CONTROLS (MODEL 202-1)

(1) POWER Press-light Switch	Turns power on or off to module. Lights when power is on.
(2) PROGRAM MODE Selector	Selects mode of operation for controlling the column-oven temperature.
(3) INITIAL TEMPERATURE Control	Sets initial or starting temperature of program. Also sets isothermal temperature of column oven when temperature programming is not used.

(continued)

TABLE VII-8
PILOT PLANT OPERATING INSTRUCTIONS
PROCESS DESCRIPTION, FLOWSHEET IDENTIFICATION

Stripping gas enters at the top and leaves at the bottom of the reactor, passing in turn through a sulfur condenser, demister, sulfur knock-out drum and a line filter where the gas is cooled and sulfur is recovered. Moisture is removed from the gas in a gas dryer containing molecular sieves (when the sieves become wet, the gas is switched to the second dryer where the wet sieves are regenerated with hot air). Gas leaving the dryer is pressurized in the stripping gas compressor. Compressed stripping gas is metered, heated and returned to the SO_2 reactor being stripped.

Flue Gas Generation Section (Figure IV-10)

Sulfur-containing coal is fed to the combustion section of the combustor-cooler unit where it is burned with air. The flue gas produced is cooled in the cooler section where heat is removed by a cooling air fan. The gas is further cooled in passing through the water cooled trim cooler. Fly ash is removed from the flue gas in a cyclone separator and a filter before the gas enters the SO_2 reactor. The filters can be bypassed.

H_2S Generation Section (Figure IV-17)

The second reaction takes place at high temperature in a catalyst bed contained in the H_2S reactor. Liquid sulfur and water are fed through metering pumps into the feed preheater with natural gas. The mixture of H_2S and CO_2 produced is fed to the SO_2 reactor where it is mixed with the entering flue gas.

Instrumentation & Controls (Figure IV-18)

Most of the major controls are located on the panel board shown in the drawing as follows:

Temperature recorder: TR-7 provides a permanent record of up to 12 important process temperatures.

Multipoint temperature indicator (on adjacent panel board): MTI-9 Indicates up to 10 important process temperatures.

TABLE VII-8

PILOT PLANT OPERATING INSTRUCTIONS

PROCESS DESCRIPTION, FLOWSHEET IDENTIFICATION

A SULFUR RECOVERY PROCESS FOR CONTROLLING SULFUR DIOXIDE EMISSIONS

OBJECTIVE

The objective of this work is to develop a process for removing SO_2 from flue gas by addition of H_2S to produce sulfur and water in a vapor phase catalytic reaction.

The reactions are:

$$2\ H_2S + SO_2 \longrightarrow 2\ H_2O + \frac{3}{X}\ S_X$$

and

$$\tfrac{1}{2}\ CH_4 + \frac{2}{X}\ S_X + H_2O \longrightarrow 2\ H_2S + \tfrac{1}{2}\ CO_2$$

DESCRIPTION OF THE PROCESS

SO_2 Reduction System (Figure IV-14)

The first reaction takes place in the catalyst bed contained in one of the two SO_2 reactors provided. The gases (SO_2-containing flue gas plus H_2S from the second reaction) enter at the bottom and leave at the top of the reactor. When the catalyst in the reactor becomes coated with sulfur, the gases are switched to the second reactor while the first is stripped of sulfur. (See next section.) The two reactors are thus alternated between reaction and stripping.

Sulfur Stripping System (Figure IV-15

When the catalyst in the SO_2 reactor (in reaction cycle) becomes too inactive for effective reduction of SO_2 to sulfur, the reaction is switched to the second reactor which has previously been stripped of sulfur and regenerated. Sulfur must then be stripped from the inactive bed by circulating hot stripping gas (probably N_2/H_2S mixtures) over the catalyst to vaporize the sulfur.

TABLE VII-8

PILOT PLANT OPERATING INSTRUCTIONS

PROCESS DESCRIPTION, FLOWSHEET IDENTIFICATION

Temperature indicator controllers

TC-1, TC-2: SO_2 reactor bed temperatures.
TC-3: H_2S reactor bed temperature.
TC-4, TC-5: Stripping gas dryer bed temperatures.
HTC-6: Hot oil drum temperature.

Multipoint temperature controller MTC-8: Controls temperature at up to ten process locations as shown in Figure IV-18.

Stripping gas high temperature cut-off: TA-9 indicates the gas temperature in the chromalox heater and cuts off electrical power at preset temperature level to protect heating elements.

Oxygen monitor: CI-10 indicates oxygen concentration in the flue gas to show efficiency of combustion in the combustor-cooler unit.

Flow indicators (rotameters): FI-1, FI-2, FI-3, FI-4, FI-5, FI-6, FI-7 indicate the flow rate of the gas streams as shown in Figure IV-18.

Pressure indicators: PI-A1, PI-G, PI-1, PI-2, PI-3, PI-5, PI-SG, PI-6, PI-7, PI-A2 indicate process pressure as shown in Figure IV-18.

Flow control valves: FV-1, FV-2, FV-3, FV-4, FV-5, FV-6, FV-7 control the gas to the desired gas flow rate shown on the corresponding flow indicator (rotameter).

Motor controls: On-off push buttons to operate motors as shown on Figure IV-18.

Other instruments and controls are located on or near the equipment with which they are associated and are shown in Figures IV-10,14,15,17. These include valves, pressure gauges, dial thermometers and manometers (which read the difference in pressure between two points).

Gas samples for analysis on the gas chromatograph are withdrawn through a fitting containing a rubber septum through which the needle of a hypodermic syringe can be inserted. Figures IV-14, 15, 17 show these sample points marked S-1, S-2, S-3, S-4, S-5, S-6, S-7, S-9 and S-10.

TABLE VII-8

PILOT PLANT OPERATING INSTRUCTIONS

PROCESS DESCRIPTION, FLOWSHEET IDENTIFICATION

PROCESS TEMPERATURES RECORDED, INDICATED OR CONTROLLED AT THE PANEL BOARD

TR-7 - Temperature Recorder

#1
#2 Sulfur Condenser Inlet
#3 Sulfur Condenser Outlet
#4 H_2S Reactor Bed
#5 SO_2 Reactor #1 bed
#6 SO_2 Reactor #2 bed
#7 Flue Gas Inlet
#8 Flue Gas Outlet
#9 Stripping Gas Dryer #1 bed
#10 Stripping Gas Dryer #2 bed
#11 Catalytic Incinerator Bed
#12

MTI-9 - Temperature Indicator

#1 Sulfur Condenser, lower zone
#2 Sulfur Condenser, middle zone
#3 Sulfur Condenser, upper zone
#4 Stripping gas entering SO_2 reactors
#5 Sulfur knock-out drum, inlet
#6 Sulfur knock-out drum, outlet
#7 Catalytic incinerator, inlet
#8 Catalytic incinerator, outlet
#9 Regeneration air inlet (primary)
#10

MTC-8 - Multipoint Temperature Controller

#1
#2 Catalytic incinerator bed
#3 H_2S reactor preheat
#4 Primary, regeneration air
#5
#6
#7 Primary, stripping gas
#8
#9
#10 Main Stack gas feed

TABLE VII-8

PILOT PLANT OPERATING INSTRUCTIONS

PROCESS DESCRIPTION, FLOWSHEET IDENTIFICATION

Flowmeters

FI-1	Natural Gas to Combustor
FI-2	Primary Combustion Air
FI-3	Secondary Combustion Air
FI-4	Natural Gas to H_2S Generator
FI-5	Stripping Gas
FI-6	Incinerator Auxiliary Air
FI-7	Dryer Regeneration Air

TABLE VII-9

PCR MEMO ON COAL COMBUSTION OPERATION

TO: N. J. Weinstein

FROM: A. T. Goding

SUBJECT: Visit to General Ionics Plant, Bridgeville, Pa. on March 19, 1969

Progress in firing the gas burner required to preheat the combustion furnace was discussed with J. W. Seehausen and H. A. Mintert. The first successful firing had been accomplished the day before by removing the nozzle from the burner. This apparently reduced gas velocity at the nozzle tip sufficiently to prevent flame out - a condition in which the flame fails to propagate back to the burner tip.

Operation of the burner was demonstrated by setting the burner in a temporary arrangement of firebrick resembling the geometry of our combustion chamber. Ignition was accomplished on the first attempt by thrusting a gas torch into the chamber, actuating the flame sensor through the usual firing sequence. While the flame was somewhat unstable at first, as the fire brick became hot, the flame improved until it was in contact with the burner tip most of the time. Under these conditions, the flame appeared to be very hot.

Mr. Glen Reynolds, a combustion specialist from the Pittsburgh office of North American (Combustion Controls) Co. arrived and made some adjustments on the controls. Flame-out occurred when the air pressure to the gas mixer was increased too far. He said this was caused by the restricted port area for gas-air mixture leaving the burner tip even with the nozzle removed. Unfortunately, the opening cannot be further enlarged because of limited space at the burner tip. Mr. Reynolds said that flame stability would be best with a rich gas mixture.

I was taken to the Bruceton Facility of the Bureau of Mines where I was introduced to Mr. Roy C. Kurtzrock who directs development projects based on coal combusion. Messrs. Kurtzrock, Seehausen, Mintert and I had a very helpful question and answer session in which burner design, gas and coal combustion and coal feeding were discussed. Some ideas, mostly corroborated by Bureau of Mines operating experience were:

Coal Feeding

1. At least 30 ft./sec. gas velocity is usually required to transport coal containing 70% of smaller than 200 mesh particles. Since this may be close to the velocity where flashback may occur, slightly higher velocities are recommended. 50-60 ft./sec. velocities are used for vertical transport of powdered coal.

2. Vibration of coal transport lines is recommended.

TABLE VII-9

PCR MEMO ON COAL COMBUSTION OPERATION

3. Coal should be as dry as possible for trouble-free feeding. Maximum recommended moisture content is 2%. Our coal analysis shows 4.5% moisture. If we experience problems, drying may be required.

Coal Combustion

1. A wall temperature in the combustion chamber of about 2000°F will insure positive ignition of a coal-air mixture. This is determined by eye or by use of a pyrometer. Commercial units run with 20% excess air, but B of M has run with as little as 5-10% excess.

2. The greater the turbulence, the shorter will be the flame. Preheating of secondary air should help in keeping flame closer to the burner tip.

3. Primary air, that used to transport coal through the burner, comprises 25-30% of the total air flow in commercial burners and up to 50% on pilot plant units operated at B of M. Secondary air, introduced through a separate port at the burner tip, provides additional air needed for combustion and imparts turbulence to the flame. The 4 lb./hr. unit operated by B of M, uses a third air stream to obtain better flame characteristics. This feature was not incorporated into our design.

4. Burner tip arrangement consists of a central pipe for gas-air mixture and two concentric annular ports of increasingly larger diameter. Primary air plus coal will flow from the smaller annular ring at a velocity of 27.5 ft./sec. Secondary air leaves the outer annular ring at 45 ft./sec. This assumes design air flow of 20 SCFM at a burner tip temperature of 600°F and split 25%/75% between primary and secondary air.

5. Procedure for firing coal flame:

   a. Preheat furnace by gas combustion

   b. Shut off gas flame and set flows of primary and secondary air on rotometers.

   c. Start feeding coal which will ignite from the hot walls.

6. U.V. sensor is not sensitive to coal flame and is not used during coal combustion.

7. Control of combustion is done by monitoring O_2 content of the flue gas. O_2 concentration normally does not vary more than 0.5% when stable air and coal feed rates have been established.

Mr. Kurtzrock said that their major problems were:

1. Feeding coal at a constant rate with a minimum of pulsation.

TABLE VII-9

PCR MEMO ON COAL CUMBUSTION OPERATION

2. Slag build up in the combustion chamber.

Ionics will reposition the flame sensor, add a slight port and install new fire brick in the burner. They plan to deliver and start up the unit early next week.

Before leaving Bridgeville, I was introduced to Mr. Daniels who is Vice President and General Manager of General Ionics Division. He offered continued assistance in obtaining satisfaction on their equipment.

A. T. Goding

A. T. Goding

ATG:iod

TABLE VII-10

COAL CHARACTERISTICS

Supplier: Christopher Coal Company, Division of Consolidation Coal Co., Osage, West Virginia

Size and Analysis Before Size Reduction:

- 3/8" x 0 raw slack coal from Arkwright, W. Va.
- M = 4.44%
- V.M. = 36.90%
- F.C. = 46.60%
- Ash = 12.00%
- Sul. = 3.25%

Grinder: Penn Rillton Co., Florham Park, N. J. 07932

Size and Analysis After Size Reduction:

- + 100 mesh 4.0% (Expected distribution, not checked)
- - 100 + 200 mesh 27.2%
- - 200 mesh 68.8%
- Weight loss @ 110°C = 0.3 - 0.7%
- C = 71.82% (Galbraith Laboratories, Knoxville, Tenn.)
  H = 5.06%
  N = 1.29%
  S = 4.24%

FIGURE VII-1: H_2S ABSORPTION ASSEMBLY FOR SAMPLES >100 ml.

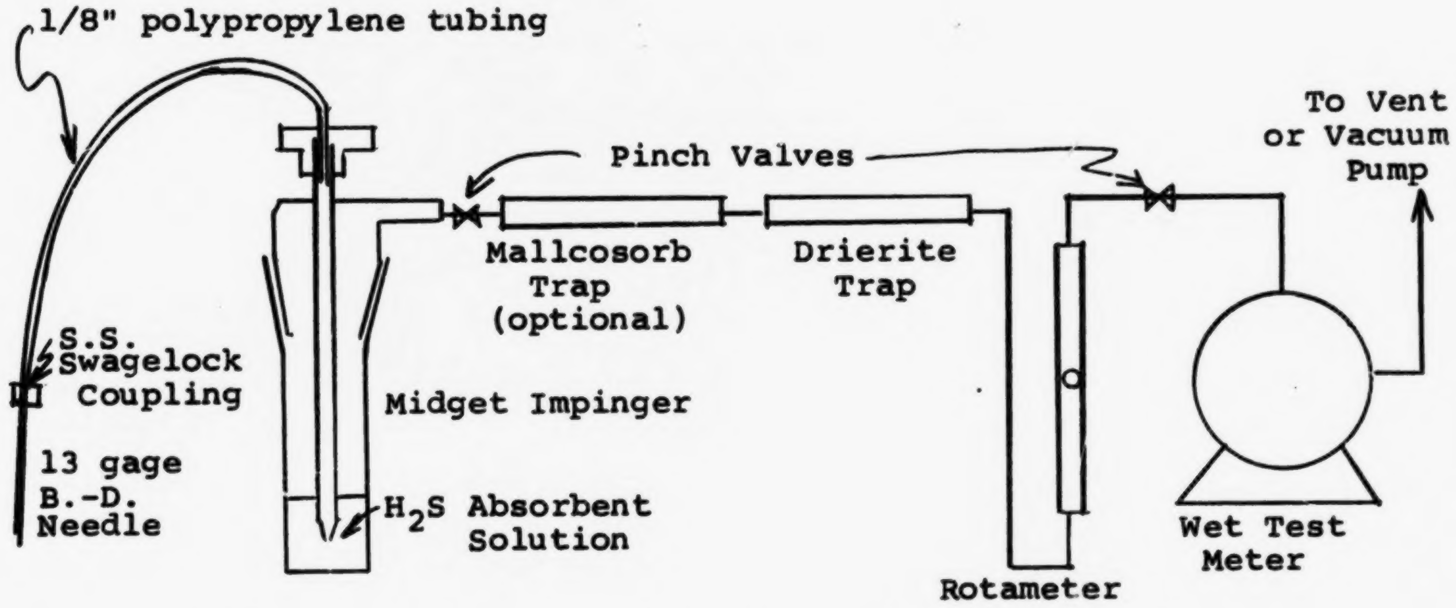

1/8" polypropylene tubing
Pinch Valves
To Vent or Vacuum Pump
Mallcosorb Trap (optional)
Drierite Trap
S.S. Swagelock Coupling
Midget Impinger
13 gage B.-D. Needle
H_2S Absorbent Solution
Wet Test Meter
Rotameter

FIGURE VII-2: H_2S ABSORPTION ASSEMBLY FOR SAMPLES <100 ml.

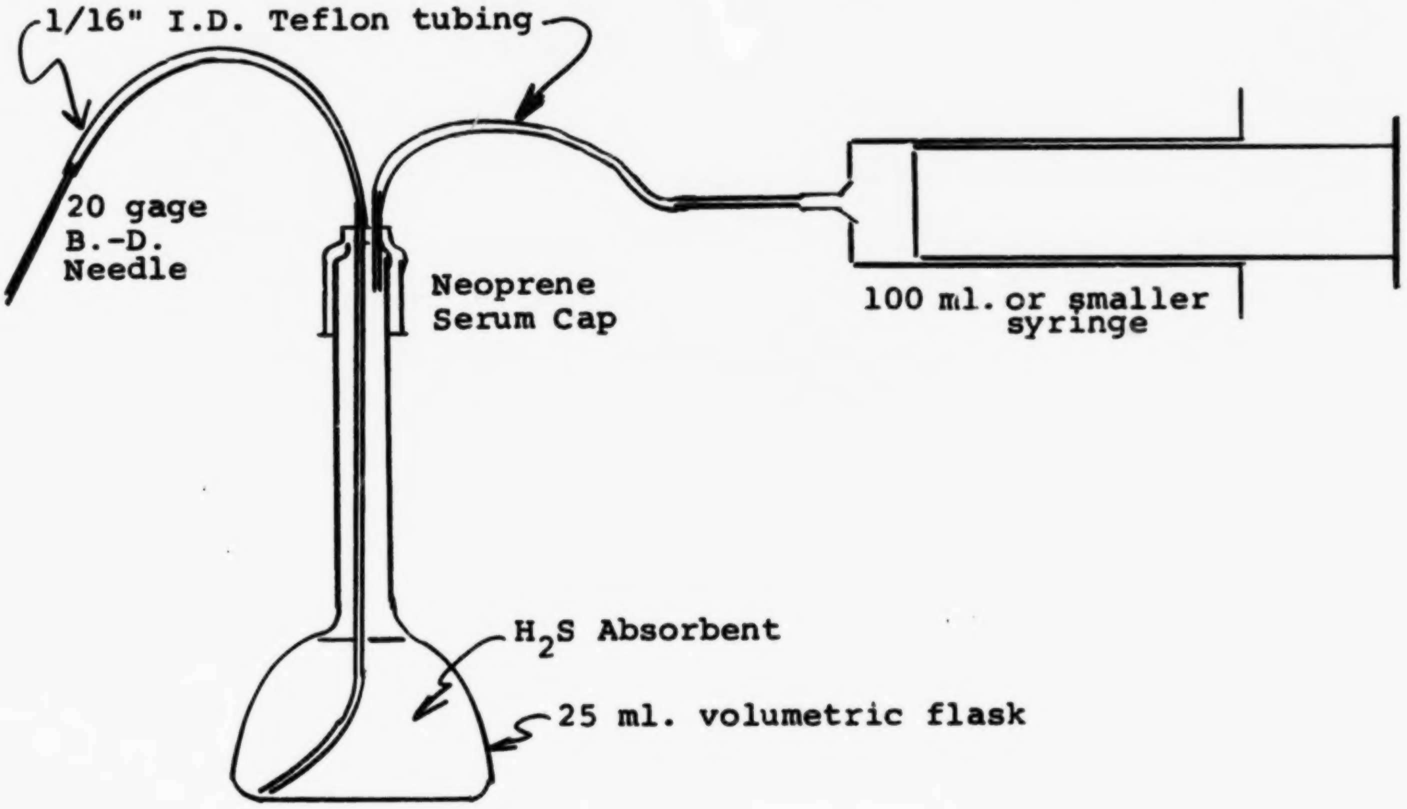

1/16" I.D. Teflon tubing
20 gage B.-D. Needle
Neoprene Serum Cap
100 ml. or smaller syringe
H_2S Absorbent
25 ml. volumetric flask

FIGURE VII-3: APPARATUS FOR NO_x SAMPLING AND ABSORPTION

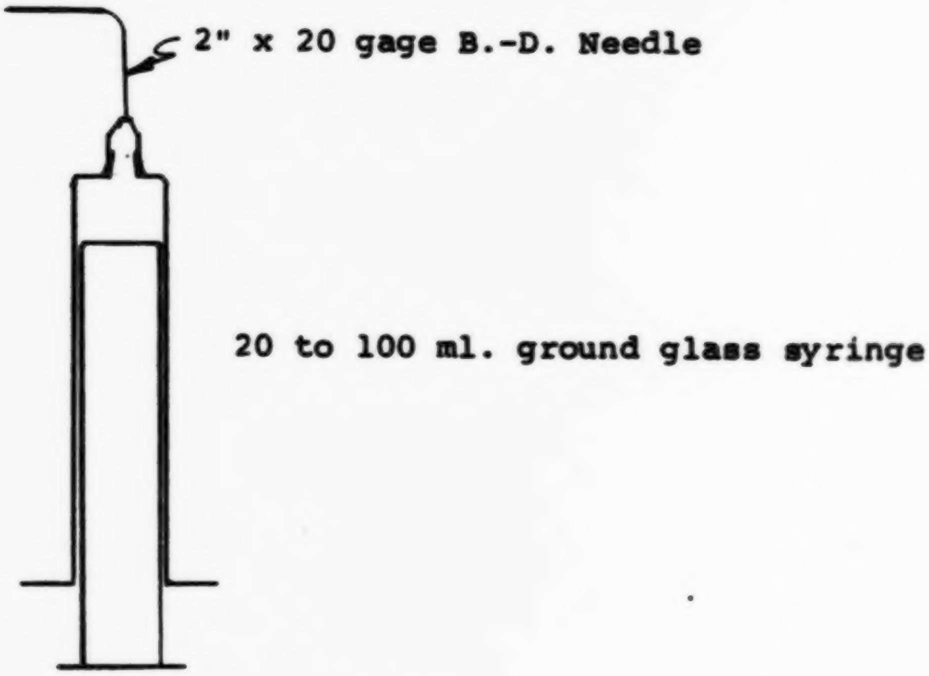

2" x 20 gage B.-D. Needle
20 to 100 ml. ground glass syringe

FIGURE VII-4: NO_x ABSORBER WITH H_2S TRAP

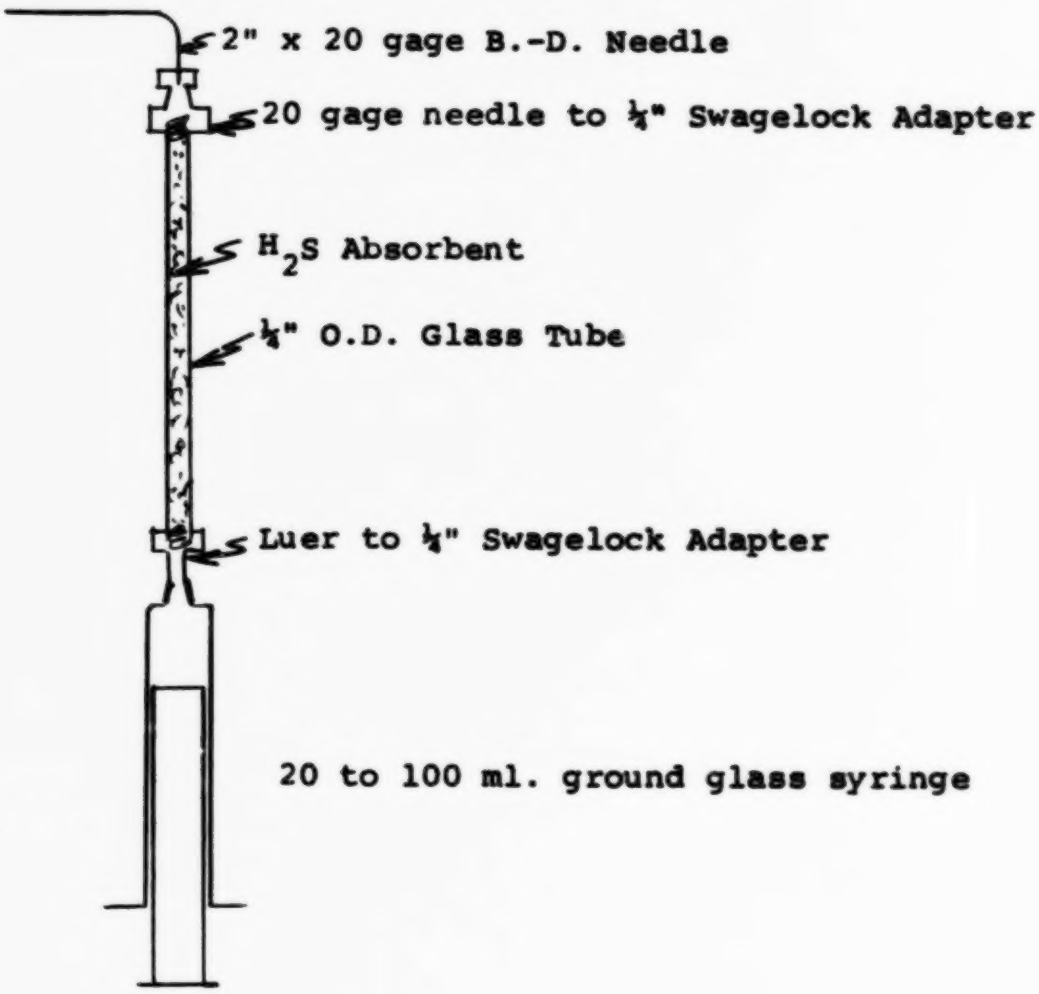

2" x 20 gage B.-D. Needle
20 gage needle to ¼" Swagelock Adapter
H_2S Absorbent
¼" O.D. Glass Tube
Luer to ¼" Swagelock Adapter
20 to 100 ml. ground glass syringe

FIGURE VII-5 QUANTITATIVE TRANSFER OF MICROVOLUMES OF PURE NO

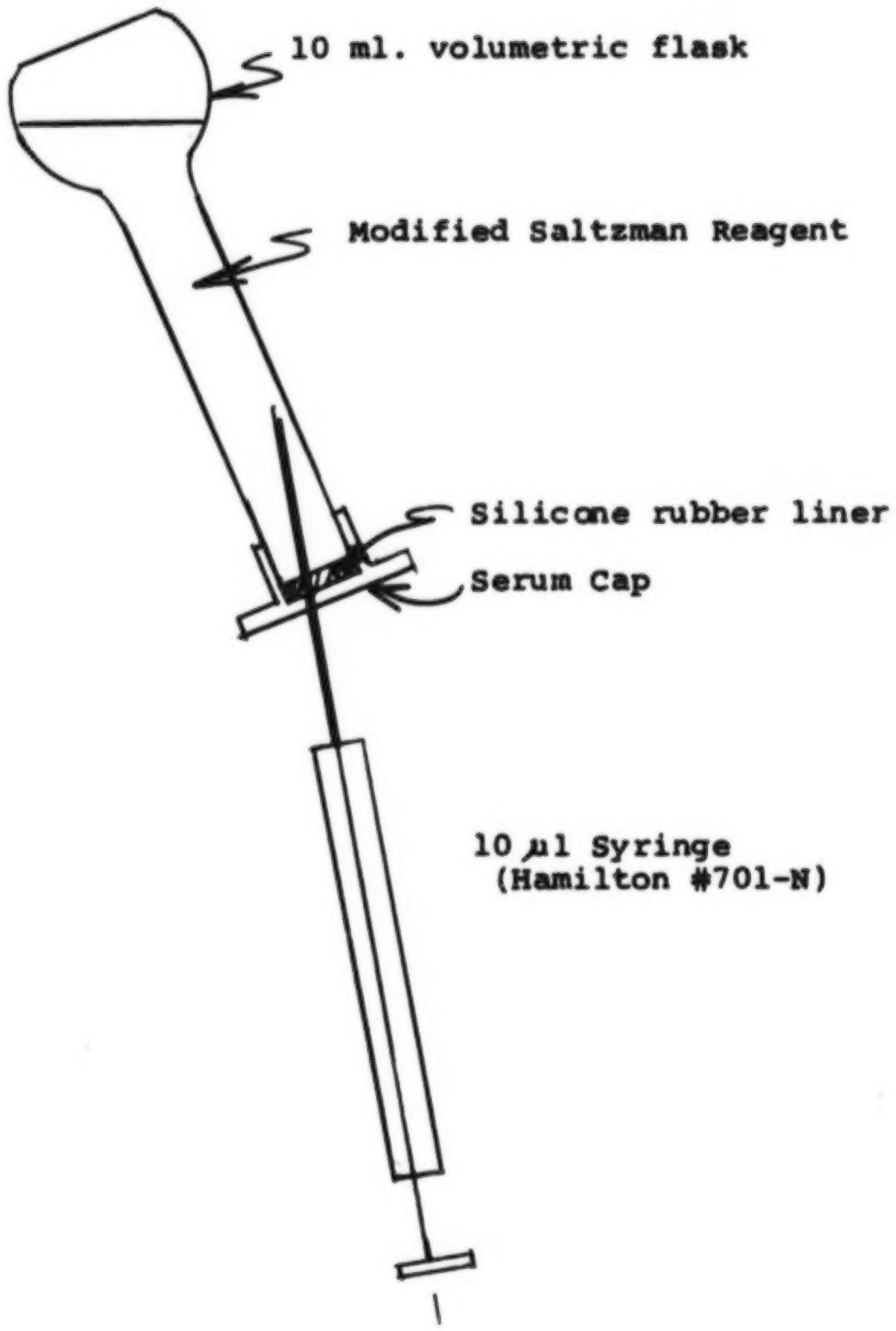
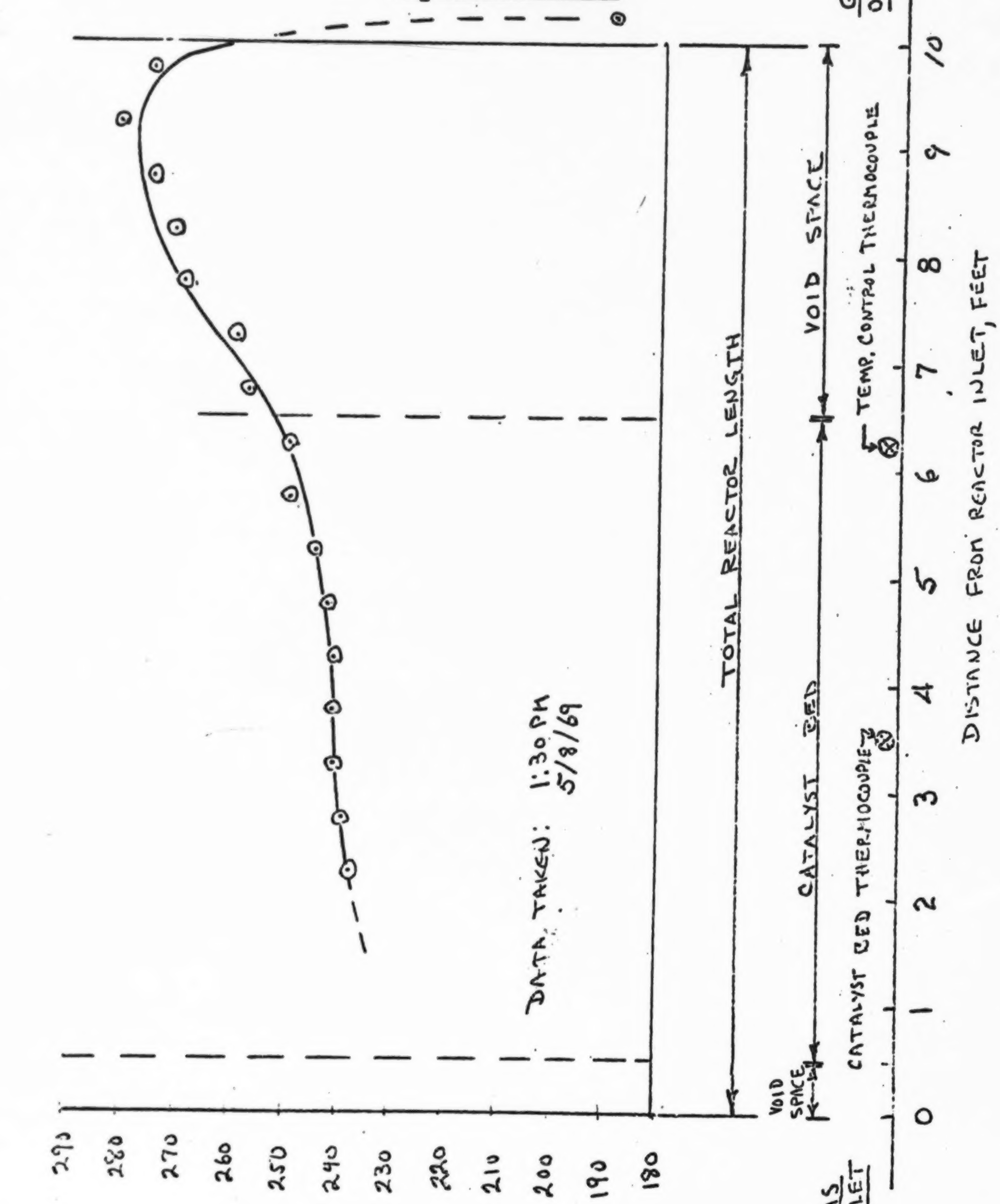

10 ml. volumetric flask
Modified Saltzman Reagent
Silicone rubber liner
Serum Cap
10 µl Syringe
(Hamilton #701-N)

FIGURE VII-6

AXIAL TEMPERATURE PROFILE

SO_2 REDUCER NO. 2


AXIAL REACTOR TEMPERATURE, °F
290
280
270
260
250
240
230
220
210
200
190
180
DISTANCE FROM REACTOR INLET, FEET
0
1
2
3
4
5
6
7
8
9
10
GAS INLET
GAS OUTLET
DATA TAKEN: 1:30 PM 5/8/69
TOTAL REACTOR LENGTH
VOID SPACE
CATALYST BED
VOID SPACE
CATALYST BED THERMOCOUPLE
TEMP. CONTROL THERMOCOUPLE